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Note on the Structure of the Trithionate Group, $(S_3O_6)^{-2}$

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The structure of the trithionate group is found from a complete determination of the crystal lattice of the potassium compound. Two of the sulphur atoms form four bonds each, three bonds with oxygen atoms and one with sulphur. The four bonds are directed towards the corners of a tetrahedron. The third sulphur atom forms only two bonds, both with sulphur atoms; the bond angle is 103°. The S−O distance is 1.50A and the S−S distance 2.15A. Some features of the binding in sulphur-oxygen radicals are briefly discussed.

UNTIL three years ago the sulphate radical remained the only sulphur oxygen group the structure of which was known. Since then we have in this laboratory determined the structures of the sulphite,[1] the pyro-sulphite[2] and the persulphate[3] groups, while that of the dithionate[4] was found elsewhere. We are now in position to add a sixth group to this list, namely the trithionate group.

The structure of the trithionate group was obtained through a complete determination of the crystal lattice of the potassium compound. Crystals of potassium trithionate have orthorhombic symmetry. The unit cell contains four molecules and have dimensions $a=9.77\pm0.04$A $b=13.63\pm0.04$A, $c=5.76\pm0.02$A. The space group is $Pnam(V_h^{16})$. Two sets of 8 oxygen atoms are lying in general positions of the space group, while there are two sets of four equivalent potassium atoms, three sets of four sulphur atoms and two sets of four oxygen atoms all lying in the reflection planes. Thus there are 20 degrees of freedom in the crystal lattice. By suitable methods of attack and somewhat tedious calculations we succeeded in determining the values of all 20 parameters with considerable accuracy (see Table I).

TABLE I. *Parameter values.*

	$2\pi x$	$2\pi y$	$2\pi z$		$2\pi x$	$2\pi y$	$2\pi z$
K_I	47°	32°	90°	O_I	−45°	110°	90°
K_{II}	65	−85	90	O_{III}	125	210	90
S_I	12	115	90	O_I'	30	100	15
S_{II}	30	170	90	O_{III}'	130	150	15
S_{III}	110	170	90				

In agreement with chemical knowledge three sulphur atoms and six oxygen atoms are grouped together in the lattice so as to form the trithionate radicals. It should be remarked that this is a direct experimental result of our investigation, as we in solving the structure did not rely upon any other chemical evidence than the result of chemical analyses.

[1] W. H. Zachariasen and H. E. Buckley, Phys. Rev. **37**, 1295 (1931).

[2] W. H. Zachariasen, Phys. Rev. **40**, 923 (1932).

[3] W. H. Zachariasen and R. C. L. Mooney, Zeits. f. Krist. (in press). Compare Phys. Rev. **44**, 327 (1933).

[4] M. L. Huggins and Glenn O. Frank, Am. Mineral. **16**, 580 (1931).

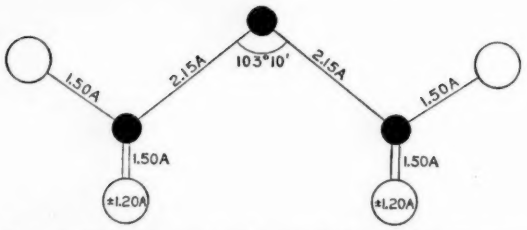

FIG. 1. The structure is shown of the trithionate group. The small circles represent sulphur atoms, the large circles oxygen atoms. Unless indicated by attached numbers the atoms lie in the plane of the paper. The connection lines indicate the bonds.

The structure of the trithionate radical is shown in Fig. 1. One will notice that the symmetry of the group is fairly high, there being two reflection planes. Only one of these planes was found for the crystal lattice as a whole, namely the plane passing through the three sulphur atoms. Two of the sulphur atoms form four bonds each, three of the bonds being with oxygen atoms and one with the third sulphur atom. The angles between the bonds were found to be practically equal to the tetrahedral angle. The third sulphur atom forms only two bonds, both with other sulphur atoms. The angle between these two bonds was found to be 103°, definitely lower than the tetrahedral angle. The distance between sulphur and oxygen is on the average 1.50A (the individual values lying between 1.42A and 1.57A). The sulphur to sulphur distance is 2.15A (individual values 2.14A and 2.17A). This last value compares favorably with the distance 2.18A found in the pyrosulphite group and the distance 2.14A found in FeS_2. In $K_2S_2O_6$ M. L. Huggins found an S−S distance of 2.06A. Also the S−O distance has been found to be essentially constant in all sulphur oxygen radicals and equal to a value somewhere between 1.45A and 1.50A.

Like all other sulphur oxygen radicals of the form $(S_mO_n)^{-2}$ the trithionate group may be satisfactorily interpreted in terms of only single electron pair bonds. Following Pauling[5] and Slater[6] we can account for the observed structure if we assume all the oxygens to be present as O^{-1}, two of the sulphur atoms to be present as S^{+2} and the third as a neutral atom. The S^{+2} ions should be capable of forming four electron pair bonds directed towards the corners of a tetrahedron, while the neutral sulphur atom may form two bonds which tend to be at right angles to each other. The fact that the observed angle between the two latter bonds is 103° instead of the predicted value of 90°, may be attributed to the repulsion between sulphur atoms and between oxygen atoms, as is apparent from Fig. 1.

A detailed account of the investigation will appear later in *Zeitschrift für Kristallographie*. A discussion of the structures of the sulphur oxygen groups in general also will be reserved for a later paper; on this occasion I shall only point out a few rules which seem to hold.

In order to explain the fact that sulphur in the sulphur oxygen groups forms one, two, three or four bonds, Pauling and Slater assume that sulphur is present as S^{-1}, S, S^{+1} or S^{+2}. In addition to the valence binding we will therefore often have ionic binding tending to increase the strength of the bond. With respect to oxygen sulphur can form two, three or four bonds as in sulphur mono-oxide, the sulphite group or the sulphate group. No group is known, however, in which only one sulphur-oxygen bond is formed. Thus we do not know the radical $(SO)^{-2}$, which would correspond to the hypochlorite group. This, of course, becomes explicable when we consider that we in this case will have ionic repulsion opposing the valence binding. (It fits in with the same principle that we have no group $(PO_2)^{-3}$ corresponding to the sulphoxylic or the chlorite groups.) It is highly significant, however, that we have groups $(S_2)^{-2}$ as in Na_2S_2.

The experimental determination of the structures shows that S−S binding occurs whenever the stoechiometric ratio permits, as if an S−S binding is preferred for an S−O bond. Thus the structure of the pyrosulphite radical was shown to be

$$\begin{array}{c} O \\ \cdot\cdot \quad \cdot\cdot \\ O:S:S:O \\ \cdot\cdot \quad \cdot\cdot \\ O \quad O \end{array}$$

rather than

$$\begin{array}{c} \cdot\cdot \quad \cdot\cdot \quad \cdot\cdot \\ O:S:O:S:O. \\ \cdot\cdot \quad \cdot\cdot \quad \cdot\cdot \\ O \qquad O \end{array}$$

[5] L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).
[6] J. C. Slater, Phys. Rev. **37**, 481 (1931).

No group is known, however, in which sulphur forms more than two bonds with other sulphur atoms (a double bond being considered equivalent to two single bonds). Furthermore, if sulphur forms two bonds with other sulphur atoms, no additional bonds can be formed, while a sulphur atom may form one S−S bond and three S−O bonds. According to this rule oxygen atoms can be attached only to the sulphur atoms at either end in a chain of sulphur atoms. This gives a nice explanation of the polythionates and of the nonexistence of groups like $(S_2O_7)^{-2}$ and $(S_3O_8)^{-2}$ and so on. The significance of this rule seems to be that we always have to consider the sulphur atom as neutral as far as binding with other sulphur atoms is concerned. That is to say: sulphur cannot form more than two bonds with other sulphur atoms (corresponding to the two unpaired *p* electrons) and if it forms two bonds with other sulphur atoms, it has become saturated. From reasoning of analogy we would expect that chlorine can only form one bond with other chlorine atoms in the chlorine-oxygen groups, and that a chlorine atom is saturated if one such bond is formed. This means that there should be no chlorine-oxygen groups involving chlorine-chlorine binding. This fits with observations, the oxides Cl_2O_3, Cl_2O_4, Cl_2O_5, Cl_2O_6, Cl_nO_6 and so on all being non-existent.

The Use of the Interferometer in the Isotopic Analysis of Water

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A method of analysis of mixtures of protium and deuterium oxides is presented. It consists in calibrating the apparent difference in indices of refraction of natural water and that containing higher concentrations of deuterium oxide, as obtained by a Zeiss water interferometer, against the corresponding differences in specific gravities. It is found that these two quantities are not proportional. The precision of measurement in the neighborhood of an experimentally determined specific gravity in a 40.06 mm cell is 0.01 percent.

IN the present state of our knowledge concerning the properties of the oxides of the two isotopes of hydrogen, the measurement of concentrations is of prime importance. For the most part methods of analysis are based upon differences in specific gravity of natural water and the sample. The float method[1] is a measurement of the temperature of a water bath that will just buoy up a vessel containing the sample for analysis, and depends upon the temperature coefficient of specific gravity. In another method the principle of the Cartesian diver is used so that the density of the water is determined in terms of the external gas pressure.[2] It has been found that the index of refraction of heavy water is considerably different from that of ordinary water.[3] This makes possible the use of the very precise interferometric methods for the determination of these differences. However, there are a number of indeterminate errors so that the measurements of Δn are not absolute. In order to utilize them for the purpose of analysis, it suffices to calibrate the instrument carefully by means of the specific gravities. When this is effected, the precision of the measurement and ease of operation make its use very desirable. The instrument we have used is the Zeiss water interferometer.[4]

This instrument has been employed frequently in the analysis of aqueous solutions and the reader is referred to the literature for general information.[5] Light from a tungsten lamp is passed through a cell with two chambers, the one containing ordinary water and the other the sample. The difference in the indices of refraction of the two liquids is compensated by turning a glass plate in the standard beam. This glass compensator is adjusted by a lever which is raised by means of a lifting screw to which a drum and scale are attached. A geometrical analysis of the light path as the compensator is changed shows that the length of path is not proportional to the reading on the drum. It has been found that

$$\Delta p = ax - bx^2,$$

where Δp is the change in light path and x the drum reading and a and b are constants to be determined for the instrument in use.[6]

Further, there is a periodic shift of the zero point due to the fact that the indices of refraction of the solution, the water standard, and the compensator are different for the different colors of light. As a result, the true fringe may have colored edges or may be so diffuse because of other colors falling over the area that recognition or measurement is impossible. As the compensator is turned, neighboring fringes will be found

[1] Lewis and MacDonald, J. Chem. Phys. **1**, 341 (1933).
[2] Gilfillan and Polanyi, Zeits. f. physik. Chemie **A166**, 254 (1933).
[3] Washburn, Smith and Frandsen, J. Chem. Phys. **1**, 288 (1933).
[4] Crist, Murphy and Urey, J. Am. Chem. Soc. **55**, 5061 (1933); Lewis and Luten, J. Am. Chem. Soc. **55**, 5061 (1933).
[5] Gans and Bose, Zeits. f. Instrumentenk. **36**, 137 (1916); L. H. Adams, J. Am. Chem. Soc. **37**, 1181 (1915); W. Barth, Zeits. f. wiss. Phot. **24**, 145 (1926); Geffcken and Kruis, Zeits. f. physik. Chemie **B23**, 175 (1933).
[6] Adams, J. Wash. Acad. Sci. **5**, 267 (1915).

more satisfactory, and if one is selected, an error of whole fringe units is made. Therefore, appropriate corrections must be applied.

Calibration of the Compensator

The compensator and scale are calibrated by using monochromatic light, the field now consisting of alternate light and dark bands throughout the whole range. If the light in one beam is retarded the fringes will be shifted and a particular fringe in the field can no longer be identified unless the change has been made very slowly and this fringe followed by continuous adjustment of the compensator. This can be done by filling both chambers of the cell with water and then adding a solution very slowly to the one chamber. The new position of the fringe corresponds to a definite number of fringes from the original setting. In order to find the number of fringes corresponding to the different positions of the drum, the usual procedure has been to take readings for every ten fringes and consider the average fringe width as that corresponding to the average position on the drum. In this way the fringe width or fringes per drum division are found for the whole range of the drum. A relation between the number of fringes and the drum reading is then sought.[7] In our case, the equations

$$N_G = 0.07402x - 2.67\times10^{-6}x^2 \quad (\lambda = 5461) \quad (1)$$

$$N_Y = 0.06850x - 2.49\times10^{-6}x^2 \quad (\lambda = 5890) \quad (2)$$

where N represents the number of fringes and x the drum setting, were accurate to 0.10 fringe up to 2500 divisions. However, when the individual fringes were measured, very much larger errors were found and were traced to a fault in the screw. This was not properly lined up, with the result that the tip described a small circle. When the line through the lever arm is perpendicular to the screw, no error results, but below and above this position, it is obvious that errors will be made. A plot of the number of fringes as a running number against the lower scale divisions for successive revolutions of the drum shows a minimum in the curve which should be a straight line. At the upper part of the scale the line is curved upward; at the midpoint it is straight. This is illustrated in Table I. Maximum errors of 0.15 fringe are possible because of this fault in construction. It may be possible that other workers have overlooked this source of error. In order to eliminate the difficulty, it was necessary to read the position of every fringe throughout the range of the compensator. These readings can be duplicated to 0.2 division or 0.013 fringe if the proper procedure is followed to eliminate back lash in the screw, which amounted to 1.5 divisions.

Table I.

x	Fringe width	x	Fringe width
110.2	14.0	2525.7	15.7
124.9	14.7	2541.8	16.1
139.0	14.1	2558.2	16.4
152.3	13.3	2575.2	17.0
165.2	12.9	2592.9	17.7
178.6	13.4	2509.0	16.1
192.0	13.4	2524.9	15.9
206.0	14.0		

The Skipping of Fringes

This phenomenon is conveniently observed if water is put into both chambers of the cell and a solution very slowly run into the one. The achromatic band will shift but it can be kept in view by the adjustment of the compensator. As the electrolyte is added, it is observed that the fringe is no longer achromatic but the edges become increasingly colored until this fringe has the same appearance as the neighboring fringe. With further addition of electrolyte, this neighboring fringe becomes achromatic so that an error of one full fringe is made if this fringe is selected as it must be in actual practice.

The frequency of this shift can be calculated if all the necessary data concerning the indices of refraction are available. For potassium chloride solutions it has been found by experiment to occur every 280 divisions, and for mixtures of protium and deuterium oxides, every 50 divisions. The correction in the latter case is thus almost one-third of the total reading. In order to determine where the changes actually take place, a sample of heavy water with a reading of 2300 was very slowly diluted with ordinary water and the positions noted at which pure

[7] For a variety of functions proposed, see Adams, Gans and Bose, Barth, reference 5.

achromatic fringes were observed, and again where there were two entirely similar fringes. In making these observations, it is necessary that the eye be always in a position at which the dark reference bands are free from color. From these data, Table II was constructed. In the

TABLE II.

Number of fringes skipped	Scale reading	Fringe width sodium *D* line	Total correction
1	35	14.63	14.63
2	85	14.68	29.31
3	135	14.74	44.05
4	185	14.79	58.84
5	240	14.85	73.69

third column are listed the fringe widths for sodium light. In the second column are the scale readings around which two similar fringes will be found, the higher fringe being the one read. If, for example, this were at 190 divisions, then the true fringe would be at $190-58.8=131.2$. The ratio of this corrected scale reading over the difference in specific gravity will give a constant that can be used for approximate work. Because of the inaccuracies in the screw it is desirable to use another method.

From the calibration of the compensator, using green light (λ5461), it is found that the scale readings are related to the fringes as follows:

$$\begin{aligned} 0 \text{ to } 1.8 &= 0.131 \text{ fringes} \\ 1.8 \text{ to } 178.6 &= 13.000 \quad " \\ 178.6 \text{ to } 190 &= 0.850 \quad " \\ \hline 190 \text{ div.} &= 13.980 \quad " \end{aligned}$$

Now from the ratio of the constants of Eqs. (1) and (2),

$$N_Y = 0.926 N_G \tag{3}$$

so that the number of yellow fringes would be $0.926 \times 13.98 = 12.94$ and this is in error by 4 fringes, as noted in column 1 of Table II. Thus 190 divisions correspond to 8.94 fringes of yellow light. This number is related to the difference in the indices of refraction of the water and the sample by

$$\Delta n = N\lambda/2L, \tag{4}$$

where N is the number of fringes and L the length of the cell.

CALIBRATION OF THE CELLS

The solutions for analysis were distilled twice from alkaline permanganate under atmospheric pressure and at least three times *in vacuo*. Considerable care must be observed in this latter operation to prevent spattering. The water after being frozen to evacuate the vessel is then melted in a stream of warm water with shaking. In this way the bubbles of air escape without spattering. The receiver bulb is provided with a tip which is filed and broken in the vessel to which the sample is transferred. The distillations were carried out by cooling the receiving bulb in solid CO_2 and the distilling bulb kept at about 35°C. Under these conditions, distillation took place without ebullition.

The specific gravity determinations were made in duplicate with carefully calibrated pycnometers, the usual corrections being made for temperature and barometric pressure. The pycnometers held about 28 cc except in the case of the sample containing 17 percent deuterium, where a smaller pycnometer holding about 12 cc was used. Duplicate weighings agreed within 2 parts per 100,000 which represents about 0.02

TABLE III.

Percent approx.	$\Delta s \times 10^6$	x	N	N cor.	$\Delta s/N$ cor.
Cell I. $L=40.06$ mm					
0.36	401	49.0	3.27	2.27	1767
1.20	1334	154.8	10.49	7.49	1781
2.18	2423	289.7	19.67	13.67	1772
4.41	4900	597.6	40.14	28.14	1741
14.66	16290	2103.4	133.33	92.33	1764
17.42	19356	2525.5	157.54	107.54	1800
Cell II. $L=10.06$ mm					
1.20	1334	43.5	2.90	1.90	7021
2.18	2423	65.5	4.45	3.45	7023
4.41	4900	149.5	10.11	7.11	6891
14.66	16290	498.9	33.63	23.63	6893
17.42	19356	595.4	40.00	28.00	6913
39.72	44133	1398.0	91.08	63.08	6996
Cell III. $L=1.104$ mm					
4.41	4900	12.0	0.82	0.82	5961
14.66	16290	52.6	3.52	2.52	6464
17.42	19356	59.1	3.98	2.98	6502
39.72	44133	131.5	8.89	6.89	6405

The second column is the difference in specific gravity of the sample and water at 25°C, the third is the reading on the drum of the interferometer, the fourth is the number of yellow fringes to which the drum reading corresponds, the fifth is this number of fringes less the number of fringes skipped as determined from Table II.

percent deuterium. No correction was made for possible increase of the oxygen isotopes.

The standard water was water redistilled from alkaline permanganate. A sample of this when distilled *in vacuo* showed no change when measured by the interferometer. All measurements are corrected to 25°C, the temperature coefficient of the scale readings being 0.4 percent per degree. Three cells were used with lengths 40.06, 10.01, 1.104 mm, respectively. The results are given in Table III. The last column shows that Δn as determined by this instrument is not proportional to Δs. Furthermore, as is seen in Table IV, the ratios of the Δn's for the same

TABLE IV. *Ratio of Δn's for the cells.*

Percent (approx.)	N(cor.)I/N(cor.)II.	N(cor.)II/N(cor.)III.
1.20	3.942	
2.18	3.962	
4.41	3.958	8.648
14.66	3.907	9.376
17.42	3.840	9.396
39.72		9.155
72		9.000
Measured ratio of the cells	3.982	9.11

solutions in different cells are not constant. At one position in each set the ratio is close to the ratio of the length of cells obtained by actual measurement. This effect of the length of cells has also been observed by Brodskii and Shershever.[8]

[8] Brodskii and Shershever, Zeits. f. physik. Chemie **A155**, 417 (1931).

In view of the variation in the value of $\Delta s/N$ and the non-proportionality of Δn and L it is necessary to plot $\Delta s/N$ against N for each cell and to have a sufficient number of points so that interpolation can be made with the precision desired.

The precision of Δs was shown to be $\pm 1 \times 10^{-6}$. The scale can be set to 0.5 divisions or about 0.03 fringes. The error introduced by using sodium for the tungsten light in correcting for the skipping is indeterminate but its magnitude can be estimated. There is no error if N is a whole number of skip intervals, i.e., 50 divisions or about 3 divisions since it is then simply included in the value $\Delta s/N$. There is an error for any fraction of a skip interval. The error in the constant of Eq. (3) is of the order of one or two percent. Thus the error on the maximum of three fringes would then be but a few hundredths of a fringe. Therefore, it would seem that the error in the vicinity of an experimental specific gravity value would be within 0.06 fringe. For the 40 mm cell this would represent an error of 0.01 percent of deuterium oxide. For the other cells, the error is in proportion to the length.

This method of analysis is rapid, very precise and requires small samples. After a sample is prepared free from impurities, the analysis can be made in ten or fifteen minutes. The precision is as high as can be attained by careful pycnometer methods. The minimum quantities required for analysis using the 40, 10 and 1 mm cells are 1.5, 0.3 and about 0.05 cc, respectively.

The Emission of Alkali Atoms from Various Ammonia Catalysts

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An apparatus is described for measuring the rate of emission of alkali as positive ions and as neutral atoms from the ammonia catalysts. The results show that when the temperature of the catalyst is first raised to the emission point the number of atoms leaving the surface far exceeds that of ions. In the course of several minutes heating the emissivity of atoms decays to a negligible value. Atom emission is much more persistent from catalysts containing Al_2O_3, also the temperature for equivalent ion currents is higher. Both atom and ion emission increase when sintering occurs, since the alkali can then diffuse more readily to the surface. The factors determining the ratio of atoms to ions are discussed. Under the conditions where the alkali concentration at the surface amounts to several hundredths of a molecular layer the presence of the adions will lower the work function of an appreciable fraction of the surface to a point below the ionization potential of potassium, thus permitting the potassium to escape as neutral atoms. When the alkali concentration is small, however, the work function is close to that of pure iron and the potassium can escape only in the form of ions.

A COMPREHENSIVE investigation of the physical properties of the ammonia catalysts has demonstrated that these substances are excellent emitters of positive ions of the alkali with which they are impregnated,[1] and also that the alkali concentration at the surface never builds up to more than a few hundredths of a molecular layer.[2] In the present paper this investigation is extended to a study of the conditions underlying the thermal emission of neutral atoms from these catalysts.

The experimental procedure was similar to that described previously.[3, 4] It consisted of measuring photoelectrically the amount of alkali deposited on an iron reference electrode placed beside a catalyst filament. The catalyst was heated at a constant temperature for a period of one minute with retarding or accelerating potentials for the emitted positive ions placed between it and the reference electrode. Thus when the reference electrode was positive with respect to the catalyst only neutral atoms were deposited, but when the potential was negative it received both atoms and ions. The photoelectric current from the reference electrode gave directly the amount of alkali deposited, when compared with standard emission curves.[4] In operation all the ions emitted from the catalyst reached the reference electrode. This was not true for the atoms since the geometry of the tube made it possible for only one atom in fifty to be deposited.

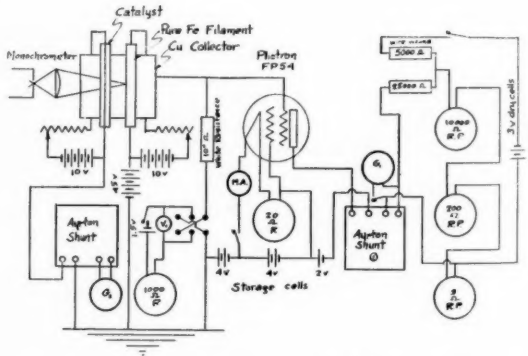

FIG. 1. As_1, 25,000 to 100,000 Ω; R.P. = Yaxley wire wound radio potentiometer; R = Yaxley radio rheostats; V_1 = Full scale 1 volt; M.A., Full scale 150 m.a.; G_1, 1 mm $= 10^{-8}$ to 10^{-10} amp.

A diagram of the apparatus is shown in Fig. 1. It includes a simple and practical electric circuit utilizing the FP 54 Pliotron, for measuring the photocurrent.

[1] C. H. Kunsman, J. Frank Inst. **204**, 635 (1927).
[2] A. K. Brewer, J. Am. Chem. Soc. **53**, 74 (1931).
[3] A. K. Brewer, Phys. Rev. **38**, 401 (1931).
[4] A. K. Brewer, Phys. Rev. **44**, 1016 (1933).

The catalyst filaments were prepared in the usual manner, care being taken during the coating and reducing process not to raise the temperature over 450°C, to insure that the alkali was not evaporated before the tests were made. All filaments were approximately the same size, containing about 0.042 g of catalyst.

Results

Typical results for potassium promoted catalysts are shown in Fig. 2.

The signs at the different points represent the potential placed on the reference electrode with

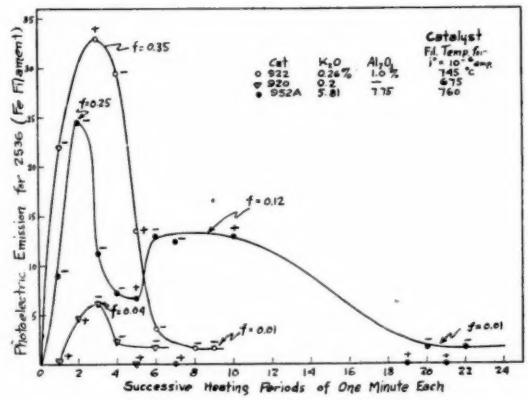

FIG. 2.

respect to the catalyst; 45 volts was used. The values of f are for the fraction of the surface of the reference electrode covered with the potassium emitted from the catalyst during a one minute heating period. After each heating period the reference electrode was restored to its original condition by glowing until the potassium deposit was completely removed.

The temperatures given are those at which the positive ion current was 1×10^{-6} amp. In the case of 920 this temperature remained fairly constant for some time; for 922 and 952 it dropped about 25° during the first few minutes of the heating period and thereafter remained fairly constant.

A comparison of the curves for 922 and 952A shows that the maximum rate of emission of atoms is smaller for the latter although the total quantity emitted is materially larger. The continuous emission of atoms from 952A is much greater than the curves illustrate since the rate of atom clean up became so slow at 760°C that from the 6 to the 20 minute periods the filament was heated at 800°C. The higher temperatures necessary for corresponding emission currents from filaments containing Al_2O_3 is doubtless intimately associated with the slowness with which these catalysts undergo sintering. Catalyst 920 reduces directly to a firm homogeneous mass, 922 does not sinter until heated to about 750°C, and 952A remains in a granular easily powdered form at all temperatures below 1000°C.

Since only one neutral atom out of fifty is deposited on the reference electrode the curves show that the emission of atoms at the maximum point exceeds that of ions by a factor of about 1000 for 922, 642 for 952A and 172 for 920. After a steady state has been established, however, the atom emission becomes less than one percent of the ion current.

A total positive ion current of 1×10^{-6} amp. corresponds to 2.43×10^{-8} g of potassium per minute. If all the potassium were given off as ions 920 would emit for 2.86×10^{3} minutes. At the maximum rate for the combined emission of ions and atoms 922 would become alkali free in about 3 minutes; when the steady state was reached, therefore, the catalyst must have been nearly alkali free.

While the results given are for positive ion currents of 1×10^{-6} amp. ion currents of the order of 10^{-14} amp. can be detected with the electrical circuit used at temperatures from 350 to 450°C depending on the type of filament. The smallness of these currents, necessarily, makes it impossible to measure accurately the ratio of ions to atoms at these temperatures. The measurements do indicate, however, that atom and ion emission begins at about the same temperature for fresh filaments. Since the atom emission decreases more rapidly with time, a worked-in filament will show very little atom emission at temperatures where the ion emission is appreciable.

Results similar to those shown above were obtained for sodium, rubidium and caesium. The general characteristics were the same as for potassium.

Discussion of Results

Becker[5] has suggested that the ratio of ions to atoms (E_p/E_A) emitted from a conducting surface may be expressed by the equation.

$$E_p/E_A = e^{(\phi - I)e/KT},$$

where ϕ is the surface work function and I is the ionization potential. Since ϕ for iron is about 4.8 volts and I for potassium is 4.3 volts $E_p/E_A = e^2 \times 10^3$, at 1000°A. This shows that the probability of an atom leaving in the neutral form is exceedingly small.

In the present experiment the conditions are complicated by the fact that the work function of the iron is changed by the presence of the potassium. The photoelectric studies of ammonia catalysts[2] show 920 and 922 to possess the properties of highly composite surfaces due to the presence of small amounts of potassium on the surface. The work function as obtained from photoelectric measurements varies over the surface from 4.8 to 2.8 volts for 920, and from 4.8 to 3.4 volts for 922; since the photocurrent for λ2800 is greatly enhanced for these catalysts over that for pure iron the work function of an appreciable fraction of the surface must be as low as 4.3 volts, hence the emission of both atoms and ions is to be expected. Since the work function increases with decreasing potassium it follows that when it rises above 4.3 volts the emission of atoms will largely cease. It is not surprising, therefore, that atom emission is appreciable only at the beginning of the heating period.

Recent experiments[3] show that potassium dissolves slowly in tungsten at 300°C and rapidly at 500°C. Similar results were obtained with iron although the solution occurs at a slightly lower temperature. As the temperature is raised the dissolved alkali diffuses to the surface and is again emitted as positive ions provided the concentration is small, and as ions and atoms if the concentration is high. The ability of potassium to diffuse through the iron increases materially with the temperature.

Previous photoelectric measurements showed the work function of iron[2] to be uneffected by the presence of alumina, hence the positive ion emissivity should be uneffected provided the concentration of alkali at the surface is the same.[6] Since the temperature for the same ion currents increases with the alumina content the rate of diffusion of alkali must be slower than for pure iron; this accounts for the difference in the temperature of emission for the two types of filaments.

The difference observed in the emission of atoms from 920 and 922 is due primarily to the difference in temperatures for equivalent ion currents. In general it is found that sintered emitters give off ions at a lower temperature than do nonsintered emitters. Thus in the case of 922, when the sintering temperature is reached the potassium is able to diffuse through the body of the catalyst and in virtue of this temperature being high it is necessarily followed by a rush of alkali to the surface. Since a small amount of alkali results in a large decrease in the work function, it follows that the chance of an atom leaving in the neutral form is enormously enhanced; for instance, if the surface is five percent covered with potassium the work function is lowered to between 3.5 and 4 volts which is well below the ionization potential of potassium. The poor diffusibility of the alkali in 952A, is largely responsible for the atom emission continuing for such a long period of time, and also for the fact that the emission never becomes large although the potassium content is high.

The writer wishes to thank Dr. C. H. Kunsman for the interest he has taken in this research.

[5] J. A. Becker, Trans. Am. Electro Chem. Soc. **55**, 21 (1929).

[6] A. K. Brewer, J. Am. Chem. Soc. **54**, 4588 (1932).

The Raman Spectra of Ring Compounds. II. Poly-Substituted Benzene Compounds

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The Raman spectra of: fluorobenzene, 1,2,4-trichlorobenzene, 1,2,4,5-tetrachlorobenzene, pentachlorobenzene, hexachlorobenzene, and hexamethylbenzene have been studied. Their relation to the vibrations of the benzene ring is discussed.

IN a previous paper,[1] the Raman spectra of chlorobenzene, bromobenzene and iodobenzene were discussed. The data on this series have now been extended by the study of fluorobenzene, the Raman spectrum of which has not been reported hitherto. The spectrum of this compound is of particular interest in that it serves as a valuable link between the spectra of the three heavier halogen derivatives which are visibly similar to each other, and that of benzene. The Raman spectra of the three dichlorobenzenes have recently been re-examined by one of us and J. W. Swaine.[2] It is the purpose of this paper to describe the results of studies undertaken to investigate the effect of further replacement of the hydrogen atoms of benzene by heavier atoms or groups, especially chlorine, upon the Raman spectrum of the benzene ring.

For this purpose, we have photographed the Raman spectrum of one compound from each of the further stages of chlorination of benzene, and that of hexamethylbenzene. While this work was in progress, a paper by Dadieu, Kohlrausch and Pongratz[3] appeared in which results were given for the entire series of chlorine derivatives of benzene and one line for hexamethylbenzene. However, as several new lines have been found for each of the compounds studied in this investigation, the description of the results at this time appears warranted.

I. EXPERIMENTAL

The apparatus and technique used in this work were described in an earlier paper.[1] All of the work was done with filtered light from capillary mercury arcs. The blue light was used in all cases, the violet when possible, and the green in a few cases. Lines of low displacement excited by the green mercury line appear in some of the plates taken primarily for the blue excitation.

All of the substances except pentachlorobenzene were obtained from the Eastman Kodak Company. Fluorobenzene was used without further purification. It is a stable liquid and required no unusual precautions. It was studied with blue and violet excitation separately. The 1,2,4-trichlorobenzene was distilled once before using, a one degree cut being taken at the reported boiling point. It was studied with blue and violet excitation separately. It is also a stable liquid but exhibits slight fluorescence which was largely eliminated by the use of a sodium nitrite filter. The 1,2,4,5-tetrachlorobenzene was distilled into the Raman tube from a small bulb without further purification. It was studied in the molten state with continuous distillation. Blue and violet excitation were used separately. Strong fluorescence was observed.

Pentachlorobenzene was prepared by the chlorination of technical tetrachlorobenzene obtained from the Dow Chemical Co. The product was purified by fractional distillation and frac-

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[1] Murray and Andrews, J. Chem. Phys. **1**, 406 (1933).

[2] Swaine and Murray, J. Chem. Phys. **1**, 512 (1933).

[3] Dadieu, Kohlrausch and Pongratz, Monats. f. Chem. **51**, 426 (1932).

tional crystallization from alcohol. Because of the small yield obtained, the purification was not complete and the purity of the resultant product was estimated to be about 93 percent. Because of the strong fluorescence and decomposition by short waves, this substance was studied only with blue excitation. It was investigated in the molten state. Hexachlorobenzene was purified by sublimation. It was studied in the molten state with continuous distillation, in the solid state and in solution in carbon tetrachloride. In the latter work, the method of High and Pool[4] was applied. Mixtures of hexachlorobenzene and carbon tetrachloride with about 1 percent of nitrobenzene or metadinitrobenzene to suppress fluorescence, were sealed into a Raman tube and the temperature raised to bring the solids into solution. The best results were obtained from the molten material, with rapid distillation to remove the colored and fluorescent decomposition products. Blue and green excitation were used separately. Hexamethylbenzene was distilled into the Raman tube without further purification and was studied in the molten state with continuous distillation. Only blue excitation was used. The fluorescence was very strong. Attempts to obtain the Raman spectrum of hexaethylbenzene were unsuccessful due to the extreme fluorescence.

II. Results

The results obtained are presented in Tables I–VI. The wave numbers of observed Raman lines in cm^{-1}, letters indicating the mercury exciting line, visually estimated relative intensities, and the Raman displacements are given. The wave numbers of the mercury lines indicated by the letters are as follows: *d*, 24,705; *e*, 24,516; *f*, 23,039; *g*, 22,995; *h*, 22,938; and *k*, 18,308. Letters following the intensities signify as follows; *b*, broad; *v*, shaded to the violet; and *r*, shaded to the red. Wave-number values enclosed in parentheses refer to doubtful lines. Most of the values reported are averages from several plates. The probable error is believed to be about 3 cm^{-1} for average lines, slightly less for very sharp lines, and about 10 cm^{-1} for extremely weak lines.

Table I. *Fluorobenzene.*

$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$
24,465	*d*	3	240	23,358	*e*	2	1158	(21,788)	*d*	1*b*	(2917)
24,276	*e*	1	240	23,293	*e*	1	1223	21,780	*h*	3	1158
24,185	*d*	2	520	23,207	*d*	1	1498	(21,719)	*d*	1*b*	(2986)
24,090	*d*	2	615	23,104	*d*	3*b*	1601	21,717	*h*	3	1221
24,000	*d*	1	(705)	22,694	*h*	8	244	21,678	*d*	1	3027
	e		516	22,436	*h*	0	502	21,636	*h*	0	1302
23,950	*d*	1	755	22,417	*h*	3	521	21,630	*d*	10*b*	3075
23,898	*d*	6	807	22,325	*h*	2	613	21,515	*d*	1	3190
	e		618	22,235	*f*	0	804	21,441	*f*	0	1598
23,875	*d*	1	830	22,185	*g*	1	810		*h*		1497
23,822	*d*	0	883	22,131	*h*	9	807	21,439	*e*	3*b*	3077
23,706	*d*	2	999	22,108	*h*	1	830	21,395	*g*	0	1600
	e		810	22,090	*d*	1	2615	21,337	*h*	4*b*	1601
23,692	*d*	10	1013	22,031	*f*	0	1008	(21,313)	*h*	0	(1625)
23,680	*d*	1	(1025)	21,984	*g*	1	1011	19,857	*h*	2	3081
	e		836	21,944	*h*	2	994	18,062	*k*	5	246
23,635	*d*	1*b*	1070	21,927	*h*	10	1011	17,503	*k*	3	805
23,546	*d*	3	1159	21,869	*h*	0	1069	17,302	*k*	3	1006
23,502	*e*	2	1014	21,836	*g*	0	1159	17,164	*k*	0	1144
23,483	*d*	3	1222								

244 (8), 502 (0), 520 (3), 615 (2), (705) (1), 755 (1), 807 (9), 830 (1), 883 (0), 997 (2), 1013 (10), (1025) (1), 1070 (1*b*), 1159 (3), 1222 (3), 1302 (0), 1498 (1), 1601 (4*b*), (1625) (0), 2615 (1), (2917) (1*b*), (2986) (1*b*), 3027 (1), 3075 (10), 3090 (1).

[4] High and Pool, Phys. Rev. **38**, 374 (1931).

TABLE II. *1,2,4-trichlorobenzene.*

$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$
24,399	*d*	2	306	23,387	*e*	0	1129	22,261	*h*	6	677
24,376	*d*	3	329	23,356	*e*	2	1160	22,182	*d*	2*v*	2523
24,249	*d*	3	456	23,332	*d*	0	1373	22,122	*h*	2	816
24,223	*d*	1*b*	482		*h*		−394	22,070	*h*	0	868
24,191	*d*	2*b*	514	23,251	*h*	0*b*	−313	21,902	*h*	4	1036
	e		325	23,136	*d*	5	1569	21,886	*h*	1	(1052)
24,060	*e*	1	456	22,756	*h*	2	182	21,849	*h*	2*b*	1098
24,029	*d*	5	675	22,740	*h*	4	198	21,807	*h*	3*b*	1131
23,891	*d*	2	814	22,722	*h*	1	216	21,780	*h*	5	1158
23,840	*d*	2	865	22,628	*h*	2	310	21,677	*h*	1	1261
	e		676	22,608	*h*	5	330	21,634	*d*	10	3071
23,668	*d*	4	1037	22,540	*h*	2	398	21,590	*d*	1	3115
23,611	*d*	2*b*	1094	22,479	*h*	2	459	21,573	*d*	1*b*	3132
23,609	*h*	1	−671	22,449	*h*	0	489	21,563	*h*	0	1375
23,575	*d*	4*b*	1130	22,423	*h*	0	515	21,445	*e*	2	3071
23,548	*d*	6	1157	22,363	*h*	0	575	21,367	*h*	5*b*	1571
23,481	*e*	2	1035		*f*		676	19,869	*h*	1	3078
23,445	*d*	1*b*	1260	22,318	*g*	0	677				
	e		1071								

182 (2), 198 (4), 216 (1), 310 (2), 330 (5), 398 (2), 459 (2), 489 (0), 515 (0), 677 (6), 816 (2), 868 (0), 1036 (4), (1052) (1), 1098 (2), 1131 (3), 1158 (5), 1261 (1), 1375 (2), 1571 (3), 2523 (2*v*), 3071 (10), 3115 (1), 3132 (1).

TABLE III. *1,2,4,5-tetrachlorobenzene.*

$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$
24,350	*d*	2	355	22,642	*g*	1	353	21,775	*h*	8	1163
24,194	*d*	0	511	22,625	*h*	3	313	21,745	*h*	1	1193
24,150	*e*	1	366	22,583	*h*	10*v*	355	21,727	*h*	1	1211
24,018	*d*	3	687	22,432	*h*	2	506	21,696	*h*	0	1242
23,827	*d*	1*b*	878	22,363	*h*	1*b*	575	21,640	*d*	3	3065
	e		689		*f*		676	21,601	*h*	1	1337
23,615	*h*	1	−677	22,315	*g*	1	680	21,557	*d*	1	3148
23,538	*d*	4*r*	1167	22,297	*h*	1	641	21,518	*d*	0	3187
23,355	*e*	1	1161	22,253	*h*	10	685	21,463	*f*	1	1576
23,289	*h*	2	−351	22,059	*h*	0*b*	879		*h*		1475
23,253	*h*	1	−215	22,014	*h*	0	924	21,455	*e*	0	3061
23,133	*d*	2	1572	21,921	*h*	0	1017	21,370	*h*	5	1568
22,747	*h*	5	191	21,872	*f*	0	1167	21,345	*h*	0	1593
22,708	*h*	3	230	21,833	*g*	0	1162	19,860	*h*	1	3078
22,683	*f*	1	356								

191 (5), 220 (3), 313 (3), 355 (10), 506 (2), 641 (1), 685 (10), 879 (0), 924 (0), 1017 (0), 1163 (8), 1193 (1), 1211 (1), 1242 (0), 1337 (1), (1475) (1), 1568 (2), 1593 (0), 3065 (3), 3148 (1), 3187 (0).

TABLE IV. *Pentachlorobenzene.*

$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$
23,280	*h*	0	−342	22,376	*h*	3	562	21,726	*h*	3	1212
22,738	*h*	2	200	22,308	*h*	0	630	21,701	*h*	0	1237
22,710	*h*	1	228	22,251	*h*	2	687	21,592	*h*	1	1346
22,661	*h*	1	277	21,985	*h*	1	953	21,545	*h*	0	1393
22,643	*g*	0	352	21,943	*h*	0	995	21,477	*h*	0	1461
22,617	*h*	2	321	21,851	*h*	1	1087	21,380	*h*	3*b*	1558
22,588	*h*	5*b*	350	21,772	*h*	3	1166	21,343	*h*	0	1595
22,551	*h*	3	387	21,749	*h*	2	1189	21,265	*h*	1	1673
22,427	*h*	0	511								

200 (2), 228 (1), 277 (1), 321 (2), 350 (5*b*), (387) (3), (511) (0), 562 (3), 630 (0), (687) (2), 953 (1), 995 (0), 1087 (1), (1166) (3), 1189 (2), 1212 (3), 1237 (0), 1346 (1), 1393 (0), 1461 (0), 1558 (3), 1595 (0), 1673 (1).

TABLE V. *Hexachlorobenzene.*

$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$
23,309	*h*	3	−371	22,534	*h*	0	404	21,366	*h*	0	1572
23,260	*h*	1	−322	22,001	*h*	0	937	21,321	*h*	0	1617
22,772	*h*	1	166	21,968	*h*	0	970	18,673	*k*	1	−365
22,717	*h*	2	221	21,924	*h*	0	1014	18,086	*k*	0	222
22,663	*h*	0*b*	275	21,754	*h*	1	1184	17,976	*k*	1	332
22,614	*h*	3*b*	324	21,712	*h*	3	1226	17,933	*k*	5	375
22,594	*h*	0	344	21,505	*h*	0*b*	1433	17,884	*k*	0	424
22,566	*h*	10	372	21,423	*h*	2	1515				

166 (1), 221 (2), 275 (0*b*), 324 (3*b*), 344 (0), 372 (10), 414 (0), 937 (0), 970 (0), 1014 (0), 1184 (1), 1226 (3), 1433 (0*b*), 1515 (2), 1572 (0), 1617 (0).

TABLE VI. *Hexamethylbenzene.*

$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$
23,488	*h*	2	−550	22,385	*h*	2	553	21,615	*h*	0	1323
22,625	*h*	0	313	22,363	*h*	1	575	21,553	*h*	0	1385
22,595	*h*	1	343	22,155	*h*	1	783	21,355	*h*	0	1583
(22,560)	*h*	0*b*	(378)	21,785	*h*	1	1153	19,999	*h*	1	2939
22,488	*h*	1	450	(21,687)	*h*	0	(1251)	(19,953)	*h*	0	(2985)
22,441	*g*	0	553	21,643	*h*	1	1295				

313 (0), 343 (1), (378) (0*b*), 450 (1), 553 (2), 575 (1), 783 (1), 1153 (1), (1251) (0), 1295 (1), 1323 (0), 1385 (1*b*), 1583 (0), 2939 (1), (2985) (0).

III. DISCUSSION

The Raman spectra of the substances studied are represented graphically in Figs. 1 and 2 together with the spectra of the other members of the series as obtained from the literature cited above. The data for benzene have been summarized, from the numerous papers which have appeared on this substance. The data for the heavier mono-derivatives are taken from our previous paper.[1] The data for the dichlorobenzenes are taken from the paper cited above.[2]

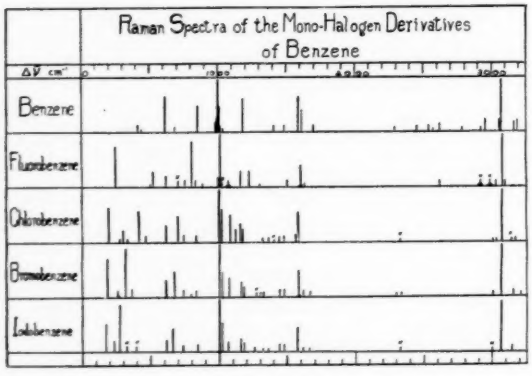

FIG. 1.

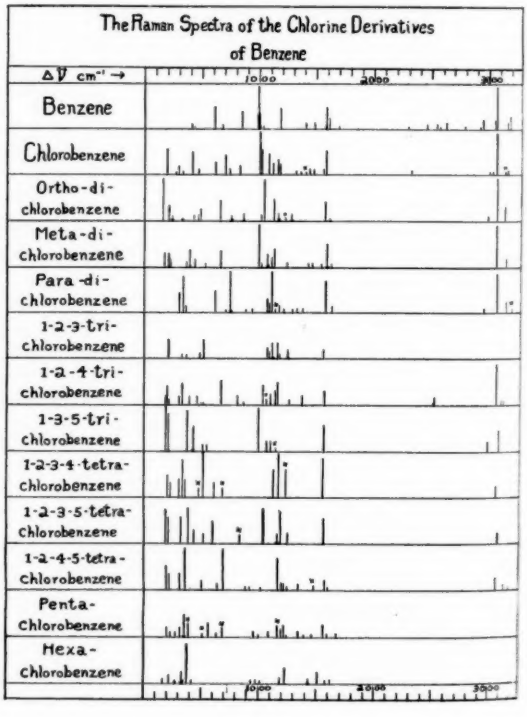

FIG. 2.

The data for the poly-substituted benzene compounds not studied in this investigation are taken from Dadieu, Kohlrausch and Pongratz.[3] The lengths of the lines represent the estimated relative intensities while a triangle at the base of the line signifies that it is broad. Cross marks above the lines designate those considered doubtful.

The Raman spectrum of fluorobenzene has not been investigated previously. The lines reported at 705 and 1025 are assumed to have been excited by the 24,705 mercury line. They coincide with the lines at 516 and 836 excited by the 24,516 mercury line but are stronger than would be expected if such were the origins. The lines reported at 2917 and 2986 coincide with the lines 1159 and 1222 excited by the 22,938 mercury line, which was not completely removed by the filter, but are assigned to the 24,705 exciting line on account of their intensity relative to lines known to have been excited by the blue mercury line.

1,2,4-trichlorobenzene has been studied by Morris[5] and by Dadieu, Kohlrausch and Pongratz.[3] The line reported at 575 and characterized as uncertain by the latter authors was not found in this investigation. All other previously reported lines were confirmed. New lines were found at 216, 489, 515, 868, (1052), 1375, 2523, 3115 and 3132. The assignment of a line to 1052 is doubtful on account of its proximity to the line 1163 excited by the 23,039 mercury line.

1,2,4,5-tetrachlorobenzene has been studied by Dadieu, Kohlrausch and Pongratz.[3] All lines reported by them have been confirmed. New lines have been found at 506, 641, 879, 924, 1017, 1211, 1242, 1337, (1475), 1593, 3148 and 3187. The assignment of the line at 21,463 cm^{-1} to 1475 as excited by the 22,938 mercury line is based on relative intensity.

Pentachlorobenzene has been studied by Dadieu, Kohlrausch and Pongratz.[3] The lines reported by them at 817 and 1028 and characterized as uncertain were not found. New lines were found at (387), (511), 630, 953, 995, (1166), 1346, 1393, 1461, 1595 and 1673. The lines listed as uncertain are those which correspond to the positions of strong lines of probable impurities and which were not found by Dadieu, Kohlrausch and Pongratz.

Hexachlorobenzene has been studied by Dadieu, Kohlrausch and Pongratz.[3] All lines reported by them have been confirmed. New lines have been found at 166, 275, 344, 414, 937, 970, 1014, 1572 and 1617.

Hexamethylbenzene has been studied by Dadieu, Kohlrausch and Pongratz.[3] These authors did not give a complete report on this substance but merely mentioned one line which corresponds to the one found at 1583. The results obtained are probably incomplete due to the very strong fluorescence.

The Raman spectrum of fluorobenzene resembles those of the heavier mono-halogen derivatives in many respects but shows certain very marked differences. It is very similar to the spectrum of toluene whose side chain has nearly the mass of the fluorine atom. All of the stronger lines below the region of 1000 cm^{-1} and some of the weaker ones are obviously analogous to lines in chlorobenzene. The group of lines near 1000 cm^{-1} resembles that in benzene rather than the grouping found in the heavier mono-halogen derivatives. The spectrum of fluorobenzene in the region of 1200 cm^{-1} is very different from those of the other derivatives. It is of interest to note that several of the lines which appear in benzene as well as in the mono-derivatives have higher values in fluorobenzene than in benzene itself while the values for the lines of the heavier derivatives are lower than those of benzene. This would appear to indicate that the introduction of the halogen has the effect of raising the force constants involved and that this effect predominates over the effect of the increased mass in the case of the fluorine compound but is overcome by the heavier masses of the chlorine, bromine, and iodine atoms.

Upon substituting additional chlorine atoms, especially in positions of low symmetry, the spectrum becomes increasingly complex. The differences between isomeric compounds of this series are marked. Little can be done at present to interpret these spectra by direct comparison. As would be expected, many lines appear in the low regions which are associated with the bending and stretching of the carbon-halogen bonds.

[5] Morris, Phys. Rev. **38**, 141 (1931).

Coincident with this is a decrease in intensity of the lines in the region of 3000 cm^{-1} associated with the C−H bond. At the same time there is a splitting up of lines due to ring vibrations caused by the loss of symmetry. As pointed out by Dadieu, Kohlrausch and Pongratz,[3] the appearance of the lines in the region of 1600 cm^{-1} in hexachlorobenzene shows that these lines cannot be accounted for by bending motions of the C−H bond. It does not, however, eliminate the possibility of lines from these motions in this region for there are several lines in this region and their inter-relations in the different compounds has not yet been traced out. The appearance of ring motions in this region would appear to indicate the presence of the double bond in the ring as pointed out by the above authors. This cannot be regarded as certain, however, for there is a possibility that such lines may be due to ring motions without double bonds and these have been observed in the mechanical models.

Dadieu, Kohlrausch and Pongratz have also pointed out the fact that the 992 line of benzene only appears in the poly-substituted derivatives in which the substituents are oriented in the meta positions with respect to each other. Lines have been found at approximately this position in the spectra of 1,2,4,5-tetrachlorobenzene, pentachlorobenzene and hexachlorobenzene but they are very weak. It is hoped that further interpretation of these spectra will be possible when studies of the mechanical models of the molecules are completed. The praseodymium nitrate used as a filter was obtained from a mixture of praseodymium and lanthanum salts kindly supplied by Mr. Mark Eichelberger of the Lindsay Light Company.

The Raman Spectrum of Arsenic Trifluoride and the Molecular Constants of AsF_3, $AsCl_3$ and PCl_3

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The Raman spectrum of AsF_3 was found to consist of four lines with the frequencies $\omega_1(1)$, 707; $\omega_2(1)$, 341; $\omega_3(2)$, 644; and $\omega_4(2)$, 274 cm^{-1}. The selection rules require a pyramidal molecule. Electron diffraction data for AsF_3, $AsCl_3$ and PCl_3 are used to establish the bond angles. The entropies of the three trihalides were calculated, and the standard free energies of formation of $AsCl_3(l)$ and $AsCl_3(g)$ were determined to be $-65{,}190$ cal. and $-62{,}718$ cal., respectively, at 25°.

INTRODUCTION

THE volatile fluorides have not received much attention with respect to their molecular structures and thermodynamic properties. Since fluorine[1] is extremely electronegative in character, it is of considerable interest to determine how this behavior is reflected in internuclear distances and binding forces. Furthermore, no readily reversible reactions involving fluorine have yet been found, and it becomes accordingly necessary to resort to indirect methods to evaluate entropies and free energies. In this paper are described the results of a study of arsenic trifluoride with respect to such considerations. For comparison, the properties of the trichlorides of arsenic and phosphorus are included.

EXPERIMENTAL

Arsenic trifluoride (B.P. 63°) was prepared by distilling a mixture of arsenic trioxide, calcium fluoride and concentrated sulfuric acid.[2] The resulting material was fractionated in vacuum in an all-glass apparatus and then vacuum-distilled into the Raman tube. It was found that the trifluoride does not attack glass so readily when moisture is excluded. An appreciable pressure of silicon tetrafluoride does develop during the course of a day, however, and the liquid trifluoride slowly becomes turbid. It was observed that considerable triboluminescence develops if a tube containing the compound is placed in liquid air and then removed and allowed to warm.

Fair photographs of the Raman lines were obtained in ten minutes and excellent ones in half an hour. The mercury-arc lamp used consisted of a long (30 cm) narrow U-tube of 8 mm Pyrex tubing equipped with electrodes sealed in at right angles near the open end. By means of a stopper and wax the lamp was enclosed in a glass jacket through which water was circulated. This type of lamp burns equally well in a vertical or nearly horizontal position; and, since it is kept cool with water, the Raman tube itself does not require cooling.

Electron diffraction experiments were made on AsF_3 and $AsCl_3$ by Dr. L. O. Brockway of this Laboratory, and we are greatly indebted to him for the results. A detailed account of the investigation will be published later by Professor Pauling and Dr. Brockway.

EXPERIMENTAL RESULTS AND DISCUSSION

In Table I are presented the results of the experiments together with various derived quantities. The Raman frequencies for $AsCl_3$ and PCl_3 are due to Bhagavantam[3] and the internuclear distances for PCl_3 to Wierl.[4]

The fluorides are generally assumed to be highly ionic in character, and this might lead to the supposition that the fluoride ions in arsenic

[1] Yost and Hatcher, J. Chem. Ed. **10**, 330 (1933).

[2] Ruff, *Die Chemie des Fluors*, p. 27, Julius Springer, Berlin, 1920.

[3] See Kohlrausch, *Der Smekal-Raman-Effekt*, p. 195 Julius Springer, Berlin, 1931.

[4] Wierl, Ann. d. Physik [5] **8**, 521 (1931).

TABLE I. *Raman frequencies and molecular constants of AsF_3, $AsCl_3$ and PCl_3.*

	$\omega_1(1)$ (cm^{-1})	$\omega_2(1)$ (cm^{-1})	$\omega_3(2)$ (cm^{-1})	$\omega_4(2)$ (cm^{-1})	$M-x$ (A)	$X-X$ (A)	ϕ	β	I_1 ($\times 10^{40}$)	I_3 ($\times 10^{40}$)	S^*_{298} (cal./deg.)
AsF_3	707(10)	341(2)	644(9)	274(4)	1.65	(2.47)	(60°)	(97°)	192.0	36.3	73.9±1
$AsCl_3$	410(10)	193(6)	370(6)	159(8)	2.20	3.27	59	96	625.4	93.3	84.0±3
PCl_3	510(10)	257(10)	480(2)	190(10)	2.04	3.18	64	101	590.4	31.7	78.6±2

Numbers in parentheses adjoining frequency values are relative intensities. Numbers adjoining the ω's are multiplicities. $M-X$ = Distance between As or P and halogen nuclei. $X-X$ = Distance between halogen nuclei. ϕ = Angle between altitude and edge of pyramid. β = Bond angle formed by two halogen atoms and As or P. I_1 = Moment of inertia about symmetry axis. $I_3 (= I_2)$ = Moment of inertia about axis ⊥ symmetry axis. S^*_{298} = Virtual entropy of vapor at 25° and one atmosphere.

trifluoride would so repel each other that they would lie in the same plane as the central arsenous ion. Since, however, four distinct Raman lines are observed, the selection rules[5] exclude the plane structure.

It seems, then, that either the electric field about the central atom is not spherically symmetric, or that the bonding is not as extremely ionic as might be supposed. The assumption of extreme ionic character suggested that, since the trifluoride has many nonpolar properties, the substance was a polymer. Careful vapor density measurements yielded a molecular weight of 133.4. The formula weight is 131.96; hence the vapor molecules are present as AsF_3. It must be concluded, therefore, that the bonding is not of the highly ionic type.

The results of the electron diffraction experiments are in accord with the assumption that the three fluorine atoms are at the corners of an equilateral triangle. Any deviation from this would lead to the splitting of the frequencies $\omega_3(2)$ and $\omega_4(2)$, which have multiplicities of two, but no splitting was observed. The experimental evidence is, therefore, in agreement with the statement that, in arsenic trifluoride, the atoms are at the corners of a regular triangular pyramid with the arsenic atom at the vertex. Similar statements apply to the trichlorides of arsenic and phosphorus.

In order to assign the observed frequencies of arsenic trifluoride to the four possible modes of vibration (two of which are double), comparisons of the spectrum with those of the trichlorides of arsenic, antimony, and phosphorus[3] were made. For the latter substances, the assignments have been based on the results of polarization experiments.

It is to be noted that the Raman frequencies for arsenic trifluoride are in all cases very close to 1.75 times the corresponding frequencies for the trichloride. This indicates that the binding constant for the As−F bond is roughly twice that for the As−Cl bond.

The F–F distance could not be determined from the results of the electron diffraction experiments. On the assumption of central forces only, Dennison[6] derived frequency formulae for the model in question, and these formulae show that the angle ϕ (see table) is a function of $\omega_1\omega_2/\omega_3\omega_4$ alone, and not of the binding constants. The value 46° was found for AsF_3, 39° for $AsCl_3$, and 51° for PCl_3. Since the two latter values are much lower than the observed ones, 59° and 64°, respectively (see Table I), it must be concluded that the formulae do not apply to the arsenic trihalides. Since the observed values of ϕ for $AsCl_3$ and PCl_3 are equal within the limits of experimental error, we have chosen to make the assumption that for the trihalides of the phosphorus group elements the bond angles are an invariant. Some small deviations may result when very large atoms, such as iodine, are involved. In accordance with this assumption we have placed $\phi = 60°$ for arsenic trifluoride.

THERMODYNAMIC CONSTANTS

When entropy calculations are based on the use of Raman frequencies, errors of as much as

[5] Debye, *The Structure of Molecules*, Blackie and Son, Ltd., London, 1932. Cf. the article by Placzek, p. 86.

[6] Dennison, Phil. Mag. **1**, 195 (1926).

3 cal./deg. may be expected when the vibrational entropy is large (10 to 20 cal./deg.).[7] In the table the uncertainties given are based on similar calculations for cases in which good heat-capacity data were available, and are meant to indicate what is believed to be the maximum possible error. In free energy calculations the resulting errors become 300 to 900 cal., which are comparable to those frequently encountered in calculations based on equilibrium data. The entropies derived from Raman spectra are often very useful, however, when it is desired to predict, with not too great precision, the tendency for reactions to take place.

The necessary thermal data for free energy calculations are available only for arsenic trichloride. The heats of formation of the liquid and vapor are 71,390 cal. and 64,030 cal., respectively.[8] The vapor pressure[9] at 25° is 11.65 mm and the entropies of chlorine[10] and solid arsenic[11] are 53.31 cal./deg. and 8.4 cal./deg., respectively, at 25° and one atmosphere. From these data there results −65,190 cal. and −62,718 cal. for the standard free energies of formation of liquid and gaseous arsenic trichloride respectively at 25°. The error in the heats of formation is some 500 cal. and that due to the entropy of $AsCl_3$ is, at most, 900 cal. The free energy values are therefore in error by some 500 to 1400 cal.

[7] Yost and Blair, J. Am. Chem. Soc. **55**, 2610 (1933).

[8] Thomsen, Ber. **16**, 39 (1883). The heat of vaporization as determined by Baxter[9] is 7360 cal. at 25°.

[9] Baxter, Bezzenberger and Wilson, J. Am. Chem. Soc. **42**, 1386 (1920).

[10] Giauque, J. Am. Chem. Soc. **54**, 1731 (1932).

[11] Anderson, J. Am. Chem. Soc. **52**, 2296 (1930).

A Relation Between Internuclear Distances and Bond Force Constants

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It has been found that for diatomic molecules the relation between the bond force constant, k_0, and the internuclear distance, r_e, is quite accurately given by the expression $k_0(r_e-d_{ij})^3 = 1.86\times10^5$, where d_{ij} is a constant depending only on the rows in the periodic table in which the two elements comprising the molecule are located. The expression holds not only for the normal state but for all excited states with a few possible exceptions. Some uses of the relation are discussed and an extension to polyatomic molecules is suggested.

THREE criteria have recently been much employed in estimating the strength and character of chemical bonds, namely, the energy of dissociation, the internuclear distance, and the so-called "force constant" of the bond, that is, the force per unit displacement which would have to be applied for infinitesimal stretching or compression of the bond. This last quantity, which in further discussion we shall call simply k_0, is in the case of diatomic molecules easily calculated from the frequency of vibration for infinitesimal amplitudes, $\omega_e c$ (which is the quantity appearing in the expression for the vibrational energy $E_{\text{vib}} = hc\{\omega_e(v+\frac{1}{2}) - \omega_e x(v+\frac{1}{2})^2\}$) by the relation $w_e c = (1/2\pi)(k_0/\mu)^{\frac{1}{2}}$.

Now since the energy of dissociation is frequently unobtainable with any accuracy the other two criteria must be employed, and it occurred to the author to find what relation might exist between them. That there is a relationship between ω_e and r_e for the various states of a given molecule has been pointed out by Mecke,[1] and Morse[2] has attempted to find a general relation whereby r_e could be approximately calculated from ω_e for any molecule. His expression $\omega_e r_e^3 = 3000$ is, however, known not to be very reliable except for a certain limited class of molecules.

In a search for a more exact expression the author treated graphically a large number of data for diatomic molecules, and in plotting k_0 against r_e soon found that within given classes of molecules a very definite relation does exist between these quantities. It was found further that if $(1/k_0)^{\frac{1}{3}}$ is plotted against r_e for all available data, for both normal and excited states, the points so obtained separate into groups, each of which falls practically on a straight line, as may be seen in Fig. 1. The points for the various states of the hydrogen molecule fall on or near the first line, those for the hydrides of the elements in the first row of the periodic system on a second, and those for diatomic molecules comprising elements each of which is found in the first row of the periodic system on still another. Evidently the class or group to which a molecule belongs depends only on the rows in the periodic system in which the elements composing it appear.

In some of the groups the data are rather meager but it appears that the best straight lines drawn through the respective groups lie practically parallel. Consequently the relation between r_e and k_0 may be represented analytically by the expression:

$$k_0(r_e-d_{ij})^3 = 1.86\times10^5,$$

where k_0 is given in dynes per cm, r_e in Angstrom units, and d_{ij} is a constant characteristic of all diatomic molecules made up of one element in the ith row and one in the jth row of the periodic system. Values for the constant d_{ij} are given in Table I.

Unfortunately data are as yet rather scanty for molecules made up of elements low down in

[1] R. Mecke, Zeits. f. Physik **32**, 823 (1925).
[2] P. M. Morse, Phys. Rev. **34**, 57 (1929).

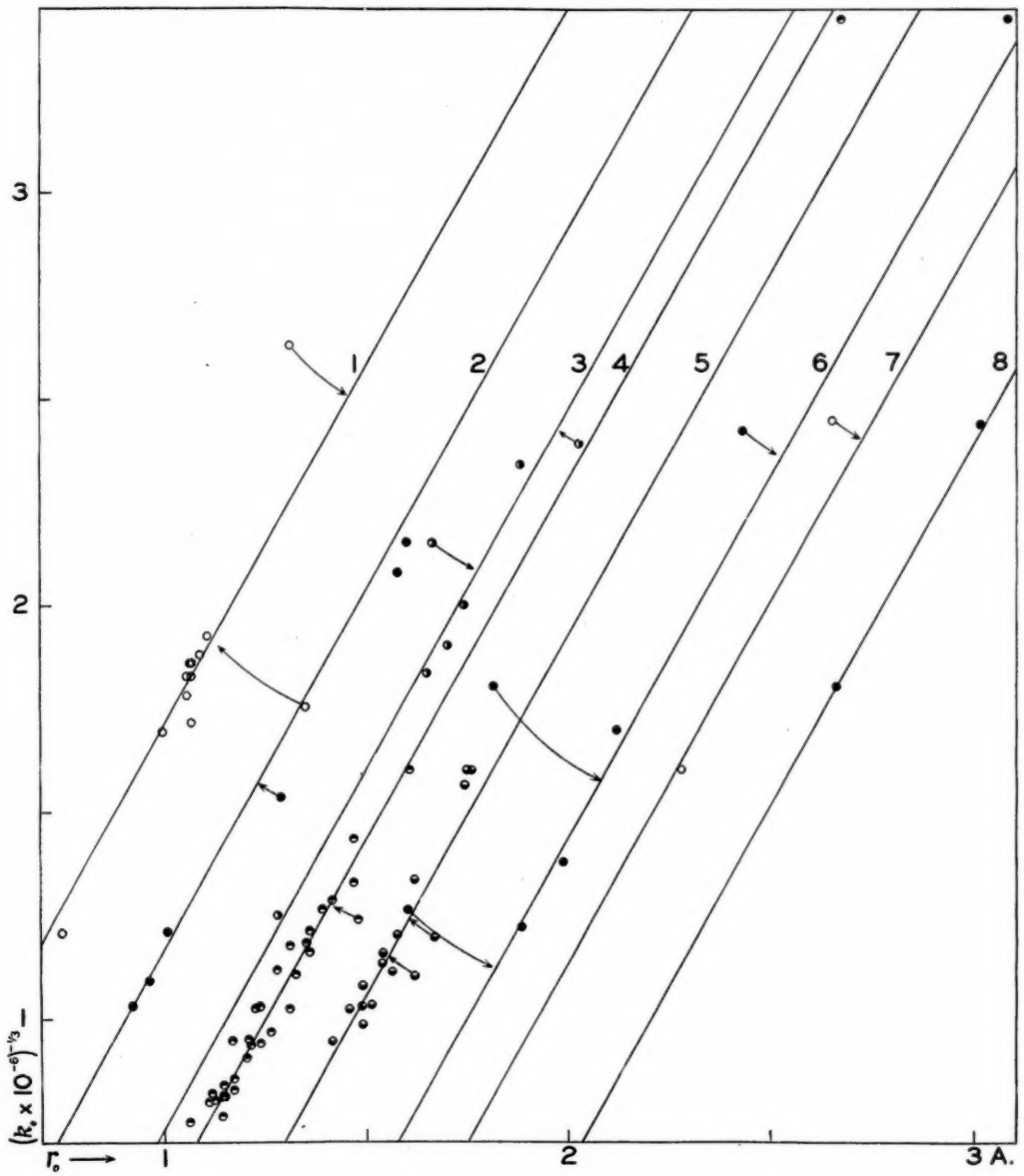

FIG. 1. A plot of the reciprocal of the cube root of the bond force constant against the internuclear distance for normal and excited states of the following molecules:

Line 1. Hydrogen
Line 2. LiH, BeH^+, OH, FH
Line 3. NaH, MgH, MgH^+, ClH, AlH
Line 4. Li_2, C_2, N_2, O_2, F_2, BeF, BeO, BO, CO, CN, NO
Line 5. PN, SiO, CS, SO, SiN, PO, AlO
Line 6. Na_2, P_2, S_2, Cl_2
Line 7. Br_2
Line 8. I_2

the periodic system, and five of the constants given were determined from data from only one molecule for each. In these cases the greatest weight was given to the normal states in estimating the constants, and it is believed that they are sufficiently accurate to be of considerable use in making predictions regarding other molecules. It will be interesting to note the behavior of elements lying in the transition portions of the long periods, when data become available, since the d_{ij}'s appear to depend on the completeness of the inner shells of the respective atoms, and

TABLE I.

Type of Molecule Atom i	Atom j	Examples	d_{ij}(A)
H	H	H_2	0.025
H	Element in row 1	HF, LiH, BeH^+	0.335
H	Element in row 2	HCl, NaH, MgH	0.585
H	Element in row 3	HBr, KH	0.650
Element in row 1	Element in row 1	N_2, O_2, NO, CO	0.680
Element in row 1	Element in row 2	CS, PN, SiO	0.900
O	Ti	TiO	0.985
O	Pb	PbO	1.125
Element in row 2	Element in row 2	Cl_2, P_2, Na_2	1.180
Cl	I	ICl	1.280
Br	Br	Br_2	1.350
I	I	I_2	1.635

not much on the outer shells. The d_{ij}'s might be called the *distances of nearest approach* of the two nuclei, and can nearly, though not quite, be taken as the sum of two radii which could be ascribed to the respective atoms. This fact, however, may be of assistance in obtaining by interpolation, constants for types of molecules for which no data exist.

It did not seem possible to indicate in the figure the molecules to which the various points belong, and a few data have not been included either to avoid confusion where the regions of different groups nearly coincided, or on account of practical limitations of size. It may suffice to say that all data which appear to make any pretensions to accuracy have been treated (with possible accidental exceptions), and to discuss the deviations in some detail, as is done in Table II, where the large deviations are specifically noted.

In group 1,1 (line 4), which includes the greater part of the really reliable data, the fit of the relation with the data is extremely satisfactory in all cases, including two excited states of the lithium molecule which fall without the limits of the diagram. Some few points in other groups which fall outside the diagram (e.g., an excited state of the sodium molecule and excited states of the alkali metal hydrides) fit somewhat less well, and in the HBr group, not shown on the plot, the deviations are considerable though not extreme. The most unsatisfactory fit is in the case of the sulfur molecule, but if the data are reliable in this case the internuclear distance is certainly so abnormally small as to be worthy of further investigation. The deviations do not appear to be systematic though there is a slight indication that k_0 may fall off more rapidly at large distances than given by the relation, so that at present it should be used with caution in regions not covered by the plot.

In the preparation of the plot some apparently large deviations were discovered to result from obvious numerical errors in the literature (for example, the internuclear distance of chlorine given by Elliot[3]), and it may not be unduly optimistic to suppose that some of the remaining

[3] A. Elliot, Proc. Roy. Soc. **A127**, 638 (1930).

TABLE II. *Deviations in r_e calculated by the relation from the experimental value.*

Group	Line in figure	Number of points with an absolute deviation (A units) <0.025	0.025–0.050	0.05–0.15	Large	Total number of points
0,0	1	8	1	1	2(A_0=90,204 99,269)	12
0,1	2	3	2	1(BeH^+)	0	6
0,2	3	4	1	2(AlH, MgH^+)	0	7
1,1	4	21	12	1(F_2')	0	34
1,2	5	8	5	3(AlO, MgF)	0	16
2,2	6	3	0	2(Na_2'', Cl_2')	2(S_2)	7

ones may be due to less apparent errors in band analysis.

Some brief comments on possible uses of the relation between r_e and k_0 may not be out of place. The most common use may be the calculation of moments of inertia or internuclear distances of molecules in case only a vibrational analysis of the bands has been made; an example is the case of antimony where the relation yields $r_e = 2.52$A, which the author believes is much more nearly correct than the value 2.21A obtained by Genard[4] from the relation of Morse.

In some cases of stellar spectra, for example, where the emitter of certain bands has not been identified it may be helpful in indicating in what part of the periodic system the atoms comprising the molecule in question are located. But perhaps the most interesting possible use is in the construction of potential functions for, and in the interpretation of the spectra of polyatomic molecules. It is not certain how well the relation will be found to hold for polyatomic molecules, since because of the difficulties involved in the extrapolation to infinitesimal vibrations there is only one case so far where an accurate value for k_0 is known. This is for CO_2[5] where the relation does indeed fit almost exactly. In other cases, where approximate values for the k_0's and the internuclear distances are known, the deviations appear to be not very large.

Two cases may be cited in which the relation will be of use even if it is only rather approximate. Sutherland[6] has recently given an interpretation of the infrared spectrum of N_2O_4 on the assumption that the molecule is plane and symmetrical, with two NO_2 groups loosely held together by a weak N – N bond. In the interpretation of certain bands which are supposed to be due to bending vibrations it is necessary to know the N – N separation. It seems improbable that this distance can be secured from electron diffraction experiments, or indeed in any other direct way, but it is possible from the spectrum to estimate roughly the stretching constant for the bond in question. From this quantity, 1.5×10^5 dynes per cm, we may estimate the internuclear distance to be around 1.75A, which leads to a ratio between two of the bending frequencies which seems to fit with experiment much better than that taken by Sutherland on the basis of an improbably small distance.

In certain other cases of molecules where both bending and elongation force constants are important in some vibrations, the interpretation of the spectra would be considerably facilitated by an approximate value of the latter which could be estimated if internuclear separations have been determined from electron diffraction experiments.

[4] J. Genard, Phys. Rev. **44**, 468 (1933).
[5] A. Adel and D. M. Dennison, Phys. Rev. **44**, 99 (1933).
[6] G. B. B. M. Sutherland, Proc. Roy. Soc. **A141**, 342 (1933).

A Quantum Theory of the Latent Photographic Image

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An explanation of the process of photographic exposure on the basis of a true photochemical reaction is offered. It is pointed out that the apparent failure of the Einstein equivalence law in the case of photographic exposure for short intervals is not real, and an equation is derived on the basis of the assumption that the *absorption* of one quantum by a sensitivity center of the grain produces an activated, but unstable state which renders the grain as a whole developable. The assumption that an activated grain may revert to an undevelopable state is an important part of the present theory, and evidence in favor of this assumption is cited. The theory that the photographic process is autocatalytic is criticized on the basis that the point of inflection of the *H* and *D* curve indicated by this theory is much higher than the point found experimentally. A preliminary treatment of the Herschel effect is given on the basis of the proposed theory, and an equation holding under special conditions is derived. The explanation of the intermittency effect as put forward by Blair and Hylan is still valid in the light of the present theory. Data taken from reliable sources are given to show that the general equation holds over wave-lengths ranging from red light to x-rays, and emulsions from Azo to Eastman Portrait.

THE quantum theory of photographic exposure, as proposed by Svedberg, Silberstein and others, has met with marked success neither in affording an equation thoroughly applicable to known exposure-density data, now in explaining such phenomena as the Herschel and intermittency effects. It is clear that a satisfactory theory, in addition to supplying an equation for the time rate of growth of density with exposure, must as well offer an explanation for the phenomena mentioned above, and for the influence of wave-length upon the maximum developable density; e.g., red light produces a much lower maximum than does blue light. Moreover, it must explain why, in the case of certain emulsions, notably the slower ones, the maximum developable density even with blue light is very definitely less than 100 percent.

The theory which, in the opinion of the present author, most closely approaches known facts is that proposed by Blair and Leighton[1] based upon the assumption that during exposure there exists an opposing tendency acting to revert exposed grains to an undevelopable condition. This assumption, in a modified form, will be retained in the present development. Evidence for the actual existence of the "reverse reaction" is furnished both by the success of Blair and his students in explaining qualitatively the Herschel and intermittency effects on this basis, and by the chemical investigations of James, Germann and Blair.[2]

PRELIMINARY STATEMENT OF THEORY

A photographically active silver halide grain contains one or more sensitivity centers, haphazardly distributed throughout the grain. The necessary and sufficient condition in order that the grain become developable is that one center *absorb* one quantum. Analogy with the photoelectric effect suggests that only a definite fraction of the quanta which strike the grain become absorbed, and that fraction rapidly decreases with the frequency until at the threshold value of ν_0, it becomes zero. The experimental work of Eggert and Noddack[3] has indicated that, of the total light absorption by the *emulsion*, a large fraction (becoming unity for long wave-lengths) is absorbed by the gelatin. It is an interesting fact that the efficiency curve of the photoelectric effect with the alkali metals is of precisely the same general nature as the corresponding curve for photographic exposure.

[1] Blair and Leighton, J. Phys. Chem. **36**, 1649 (1932).

[2] James, Germann and Blair, Reported to Colorado-Wyoming Academy of Science, Dec. 1, 1933.

[3] Eggert and Noddack, Zeits. f. Physik **20**, 299 (1923); **21**, 264 (1924); **31**, 922 (1925).

A grain which has absorbed a light quantum exists in an activated, and hence developable, albeit an *unstable* state.[4] There exists, accordingly, a tendency which may, either spontaneously or under the influence of some agent (quanta of smaller $h\nu$ are not excluded) act to revert the grain to an undevelopable condition. Moreover, the activated state of the exposed grain is smaller for smaller $h\nu$, and the probability that the grain revert to an undevelopable state is correspondingly greater. It does not necessarily follow, however, that the "undevelopable state" referred to is that of the original unexposed grain. It may be a state activated by an excess energy content smaller than a certain minimum necessary for developability. This concept may offer an explanation of the observed shift of sensitivity towards the red during exposure.

Mathematical Statement of the Theory

Silberstein,[5] by assuming random distribution of sensitivity centers, deduced a relation between the exposure and the number of developable grains. His formula, with alterations required by the present theory, is:

$$k/N = 1 - e^{\bar{\kappa}(e^{-\epsilon n\omega} - 1)} \tag{1}$$

where k = number of developable grains, N is the total number of sensitive grains in the emulsion, $\bar{\kappa}$ is the average number of sensitivity spots, ω is the average area of a sensitivity spot, n is the number of quanta falling upon the emulsion, and ϵ is a constant (only, however, for a given wave-length). Eq. (1) is valid as the expression for the forward reaction in the light of the present theory.

If $\epsilon n\omega$ (a pure number) is a small fraction, Eq. (1) yields as a first approximation

$$k/N = 1 - e^{-na} \tag{1a}$$

where $a \propto \epsilon\omega$. Eq. (1a) has ample mathematical accuracy when consideration is taken of the degree of experimental error in determining the quantities involved, and is indeed the relation which would hold rigorously if the sensitivity centers were uniformly distributed.

Eq. (1a) will be rewritten:

$$x = k/N = 1 - e^{-bt}, \tag{2}$$

where we shall define x as the developability coefficient, b is a constant, and the exposure intensity is assumed to be uniform throughout the time t. Whence, the velocity of the forward reaction tending to produce developable grains becomes:

$$(dx/dt)_f = b(1-x). \tag{3}$$

The reverse reaction tending to return the grains to an undevelopable state will, in the first approximation, be proportional to the number of grains developable at any time, and hence:

$$(dx/dt)_r = cx. \tag{4}$$

This approximation becomes poorer as x increases (see following section on Herschel effect), a point borne out by the data presented elsewhere in this article.

Combining (3) and (4), we have for the complete equation

$$\begin{aligned} dx/dt &= b(1-x) - cx \\ &= K_1 - K_2 x, \end{aligned} \tag{5}$$

where K_1 and K_2 are constants. Integrating, we obtain:

$$x = (K_1/K_2)[1 - e^{-K_2(t - A/K_1)}]. \tag{6}$$

The coefficient x will assume a maximum value $x_m < 1$ when dx/dt becomes zero. Hence, by Eq. (5) we have

$$x_m = K_1/K_2.$$

Further, when $x = 0$, $t = t_0 \leqq 0$,[6] and, from Eq. (6),

$$A/K_1 = t_0.$$

Hence, we have, substituting the above values in (6)

$$x = x_m[1 - e^{-K_2(t - t_0)}], \tag{7}$$

[4] More definite assumptions as to the nature of the "activated state" will be made at a later date. The above rather vague statement is sufficient for present purposes.

[5] Silberstein, Phil. Mag. **45**, 1062 (1923).

[6] There is evidence to support this assumption of a small but finite time lag, and it cannot be considered as introduced *ad hoc*. It must not, however, be assumed that during this period, no action is occurring, but rather that it is a period of incubation.

an equation which, although it resembles superficially that of Silberstein, differs fundamentally from the latter. The values of x_m and t_0 are read directly from the H and D curve, and the only constant to be evaluated is K_2.

Although Weigert and his co-workers,[7] studying the action of light on emulsions used in daylight photographic papers, found a point of inflection in the curve obtained by plotting time of illumination against silver which was found, Eggert and Noddack,[8] working with a similar emulsion, observed no such point. The same state of affairs exists in the data of various workers on ordinary photographic emulsions. When the time lag, t_0, is very small, the point of inflection has no definite existence. When t_0 is (relatively) large, the evidence favors the existence of an S-shaped curve. It is noteworthy in this connection that the equation of Blair and Leighton, which is based upon the assumption that the photographic process is auto-catalytic, yields as a relation between the point of inflection and the maximum developable density:

$$x_m^{-\frac{1}{2}}(1-x_m)=x_i^{-\frac{1}{2}}(1-3x_i),$$

which, when x_m is of the order of 1, yields the value $\frac{1}{3}>x_i>0.3$, a value much higher than the usual experimental one.[9]

It is, accordingly, the opinion of the author that the existence of a point of inflection in the H and D curve is an incidental, rather than a fundamental, property of the curve, and is probably in some way associated with the fundamental cause of the lag.

Preliminary Considerations on the Herschel Effect

Blair and Joehnck[10] have explained the Herschel effect on the basis of the postulated simultaneous forward and reverse reactions. If we assume, on the basis of the present theory, that light of longer wave-length than the initial exposing light, constitutes an agent which accelerates the reversal of exposed grains, we are faced with a problem presenting much greater difficulties in its quantitative treatment than the problem of initial exposure. For, although in order to make a grain developable, it is sufficient that only one developable center be formed, if the grain is to revert to an undevelopable state, *every* activated center of the grain must become passive. It has been demonstrated experimentally that the average number of activated centers per grain increases with exposure and when the initial exposure approaches a maximum this number becomes appreciably greater than one. As suggested in the preceding section, this factor would also enter into the expression for the reverse reaction as a correction term in Eq. (5), but its omission does not greatly affect the applicability of Eq. (7). In the present case, however, it is very important. We may write, then, as a more accurate expression,

$$dx/dt=b(1-x)-c(x-x_2), \tag{8}$$

where x_2 is a nonlinear function of x.

In the simplest case ($x_2=0$) Eq. (8) yields the same expression as before (Eq. (6)). The constants, however, will have different values. When $t=0$, $x=x_a$, and when $t=\infty$, $x=x_0$, the equilibrium density for the light producing the Herschel effect. Substituting these values, Eq. (6) becomes:

$$x=x_0[1+[(x_a-x_0)/x_0]e^{-K_2t}]. \tag{9}$$

For low densities, the value of x_2 will be small, and Eq. (9) will be applicable with considerable accuracy, as Table VI shows. The data for this table are taken from Table II of Trivelli's paper on *The Herschel Effect*.[11] At much higher densities, the experimental curve is markedly flatter than that indicated by Eq. (9), a condition which is to be expected in the light of the previous discussion.

Correlation of Theory and Data

There can be little discrimination between Eq. (7) and Eq. (2) in cases where x_m is of the order of 1. The obvious test of Eq. (7) is, then, its appli-

[7] Weigert and co-workers, Sitzb. Preuss. Akad. 641 (1921).

[8] Eggert and Noddack, Zeits. f. Physik **31**, 922, 942 (1925).

[9] Cf. Silberstein, Phil. Mag. **5**, 464 (1928).

[10] Blair and Joehnck, J. O. S. A. **23**, 67 (1933).

[11] Trivelli, J. Frank. Inst. **207**, 781 (1929).

cation to cases where x_m is appreciably less than one. Tables II and IV give data for two such cases.

Tables I–VI included in this article are selected from a wide range of workers and conditions. Each of the tables presented has been abbreviated by omitting (as a rule) every other value. Several additional sets of trustworthy data found in the literature (chiefly by Trivelli and Loveland and Blair) were tested by Eq. (7) and found to be in as good agreement as the data presented here. Further data both with light of longer wave-length and with slow emulsions (e.g., Azo) are greatly to be desired.

In cases when the data are expressed in terms of density rather than in terms of x, D may be directly substituted for x in the equation, since it has been shown[12] that a linear relation exists between the two.

In conclusion, as an indication of the general applicability of the theory presented, it may be pointed out that the data for x-rays and for red light satisfy Eq. (7) as well as that for blue light.

TABLE I. Eastman 40 emulsion. (Trivelli and Loveland.)

x (obs.)	x (calc.)	$E=It$	x (obs.)	x (calc.)	$E=It$
0.02	0	0.05	0.73	0.72	0.3
.07	0.08	.075	.845	.833	.4
.16	.19	.1	.935	.93	.5
.52	.53	.2			

$E_0=0.06$ $x_m=0.99$ $K=5.39$

TABLE II. Azo special emulsion. Red light. (Blair—unpublished.)

Density (obs.)	Density (calc.)	t (hours)	Density (obs.)	Density (calc.)	t (hours)
0.08	0.09	3	1.44	1.44	70
.23	.21	6	1.60	1.61	92
.71	.72	24	1.76	1.75	120
1.12	1.12	44			

$t_0=0.5$ $D_m=1.92$ $K=0.02$ $x_m=0.58$

TABLE III. Special Eastman lantern slides. X-rays. (J. Lester—unpublished.)

Density (obs.)	Density (calc.)	t	Density (obs.)	Density (calc.)	t
0.23	0.22	0.85	1.05	1.08	5.6
.27	.27	1	1.35	1.37	8.4
.42	.45	1.8	1.51	1.51	10.4
.62	.67	2.9	1.64	1.61	12.1
.80	.84	3.9			

$D_m=1.94$ $K=0.1455$ $t_0=0$

TABLE IV. Trivelli and Loveland. (Quoted by Silberstein, Phil. Mag. **5**, 483.)

x (obs.)	x (calc.)	E	x (obs.)	x (calc.)	E
0.014	0.016	1	0.276	0.274	8
.074	.071	2	.463	.444	16
.155	.153	4	.582	.588	32

$x_m=0.65$ $K=0.075$ $E_0=0.7$

TABLE V. Toy, Phil. Mag. **45**, 719. (Data read from Fig. 4.)

x (obs.)	x (calc.)	E	x (obs.)	x (calc.)	E
0.03	0.025	0.65	0.66	0.66	2.75
.11	.12	.85	.79	.77	3.6
.25	.29	1.3	.92	.87	4.8
.45	.45	1.8	.98	.95	7.0

$x_m=0.99$ $E_0=0.6$ $K=0.503$

TABLE VI. Herschel effect with infrared (Trivelli).

Density (obs.)	Density (calc.)	t	Density (obs.)	Density (calc.)	t
0.34	0.337	18	0.30	0.303	290
.34	.335	36	.29	.292	410
.33	.329	74	.28	.279	579
.32	.320	145			

$x_0=0.23$ $x_a=0.34$ $K=0.0014$

ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr. J. M. Blair and J. J. Coleman for the valuable suggestions they have made during the course of this work.

[12] Sheppard and Mees, *Theory of Photographic Process*, Arens, Eggert and Heisenberg, Veroff. wiss. Agfa **2**, 28 (1931).

On the Theory of Glass Electrodes

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A glass electrode is considered schematically to be a difficultly soluble electrolyte which absorbs water and further salts present in an adjacent solution. The potential is the distribution potential at the boundary surface between the glass and the solution. According to the theory presented this potential varies if certain reasonable assumptions are made concerning the value of the constants occurring (dissociation constants in the glass, distribution constants between glass and water) over a wide range of concentration in acid and neutral solutions in the same manner as that at an H_2 electrode. The variation of the potential differs from the latter in a strongly alkaline solution, in the manner ascertained experimentally and predicted in previous communications. The extremely simplified model describes quantitatively with one empirical constant the potentials hitherto observed. It is shown that the systems are completely explicable on the basis of the usual thermodynamic picture of equilibrium. Attempts on the other hand to describe the phenomena on the basis of diffusion potentials have not led to satisfactory results.

I. INTRODUCTION

IT is known that over a wide range of concentration electrodes of soft glass behave like hydrogen electrodes. This behavior is changed, however, in the case of electrodes of highly resistant glass. Glass of this nature may act in neutral and alkaline solutions of cations like a metallic electrode of the cation concerned.

Some time ago the writers proposed a model reproducing the behavior of both kinds of glass in all the details known at that time.[1] They furthermore predicted as a consequence of their formulae that certain intermediary types should be observable. In this successful representation by model the glass is conceived as a salt MeS which is difficultly soluble in water, and which absorbs the water and other salts of the same cation added to the solution, in solid solution.

More recently it has been found[2] experimentally that the behavior of soft glass deviates in two respects from the ideal behavior of the hydrogen electrode. In the first place, the potentials in strongly alkaline solution become dependent on the concentration of any neutral salts which may be present. In the second place, the potentials of glass electrodes differ from those of hydrogen electrodes when the solution is not an ideally dilute solution, the water activity therefore not being equal to one.

Proceeding on the assumption that the potentials at glass electrodes are diffusion potentials, Dole has attempted to give an explanation of both of these phenomena. The formulae derived by him for the first case, namely for the deviations in the alkaline range, do not fit the experiments. He therefore introduced for every series of observations a new constant in his formula and changed in every series the value of the second theoretically determined constant to obtain agreement. His formulae thus contain for each series two arbitrary constants neither of which has a theoretical meaning. Although he attempted to justify this alteration by the adduction of supplementary hypotheses, it is safe to say that his formulae can only be regarded as empirical.[3]

The deviations in the potentials of glass electrodes in concentrated solutions are not all of the same sign. Dole has explained part of the experimental observations by pointing out that the thermodynamic process at a hydrogen electrode is not necessarily the same as that at a glass electrode. At a hydrogen electrode the discharge of a dehydrated hydrogen ion may

[1] Gross and Halpern, Zeits. f. physik. Chemie **115**, 54 (1925); **118**, 255 (1925).

[2] M. Dole, J. A. C. S. **53**, 4261 (1931); **54**, 3095 (1932).

[3] Judging by the footnote at the beginning of the second paper, we take it that Dole himself is now of this opinion also.

occur while it is perfectly conceivable that hydrated hydrogen ions pass into the glass electrode.

II. Derivation of the General Formula for the Potential

We wish to show in the following pages that the scheme previously put forward by the present authors describes quantitatively without the aid of supplementary hypotheses the deviations in alkaline solution, and likewise depicts the second group of deviations, by utilizing the differences in the discharge mechanism mentioned above. To this end, however, it is necessary to carry out the calculations previously made, to a higher approximation, and, since concentrated solutions are in addition to be dealt with, simplifications permissible in the theory of dilute solutions will be avoided. We thus represent the glass by the uni-univalent salt MeS^1 which is capable of absorbing water and electrolytes in a superficial layer in solution. The distribution potential at the boundary surface concerned is then given by

$$E=(RT/F)\ \ln\ (c_k\gamma_k/c_k'\gamma_k')+\text{const.}, \quad (1)$$

in which the c and the γ denote concentrations and activity coefficients, respectively. The index k relates to any one cation for which there is distribution equilibrium, and the dashes relate to the solid phase. The diffusion potential occurring in the glass shall be neglected as small so that Eq. (1) denotes the potential of the glass electrode. We shall limit ourselves, for the sake of simplicity, to the case of *one* cation contained in the glass. The system is characterized by the symbol:

H_2O	MeS^1	HS^1	MeOH	HS^2	MeS^2	H	OH^1	$S^{1\prime}$	$S^{2\prime}$	Me
c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8	c_9	c_{10}	c_{11}
c_1'	c_2'	c_3'	c_4'	c_5'	c_6'	c_7'	c_8'	c_9'	c_{10}'	c_{11}'

The following equations are then valid for the dissociation equilibria in the liquid phase (2), in the solid phase (3), and the distribution equilibria for the non-dissociated constituents between the two phases (4).[4]

$$\frac{c_7c_8}{c_1}=K_1\frac{\gamma_1}{\gamma^2}, \quad (2_1) \qquad \frac{c_7'c_8'}{c_1'}=L_1, \quad (3_1) \qquad c_1\gamma_1=M_1c_1', \quad (4_1)$$

$$\frac{c_{11}c_9}{c_2}=K_2\frac{1}{\gamma^2}, \quad (2_2) \qquad \frac{c_{11}'c_9'}{c_2'}=L_2, \quad (3_2) \qquad c_2=M_2c_2', \quad (4_2)$$

$$\frac{c_7c_9}{c_3}=K_3\frac{1}{\gamma^2}, \quad (2_3) \qquad \frac{c_7'c_9'}{c_3'}=L_3, \quad (3_3) \qquad c_3=M_3c_3', \quad (4_3)$$

$$\frac{c_8c_{11}}{c_4}=K_4\frac{1}{\gamma^2}, \quad (2_4) \qquad \frac{c_8'c_{11}'}{c_4'}=L_4, \quad (3_4) \qquad c_4=M_4c_4', \quad (4_4)$$

$$\frac{c_7c_{10}}{c_5}=K_5\frac{1}{\gamma^2}, \quad (2_5) \qquad \frac{c_7'c_{10}'}{c_5'}=L_5, \quad (3_5) \qquad c_5=M_5c_5', \quad (4_5)$$

$$\frac{c_{10}c_{11}}{c_6}=K_6\frac{1}{\gamma^2}, \quad (2_6) \qquad \frac{c_{10}'c_{11}'}{c_6'}=L_6, \quad (3_6) \qquad c_6=M_6c_6'. \quad (4_6)$$

The activity-coefficients are assumed to be the same for all ions and equal to one for undissociated molecules with the exception of water. The activity-coefficient in the solid phase shall be independent of concentration so that the values of the L are constants. Furthermore, we have the equations of electric neutrality for both phases, as follows:

$$c_7+c_{11}=c_8+c_9+c_{10}, \quad (5)$$

$$c_7'+c_{11}'=c_8'+c_9'+c_{10}'. \quad (5')$$

[4] These equations are not all independent of each other, but we have put them all down, for the sake of completeness.

The concentration of the added acid ion is assumed to be known; furthermore according to our assumptions in regard to activity-coefficients

$$c_2' = A. \tag{6}$$

By successive substitution of the equilibria Eqs. (3_1), (3_2), (3_4), (3_6), (4_1), (4_4), (4_6), (2_1), (2_4), (2_6), (6) in the condition of electric neutrality (5′) we obtain

$$\frac{c_{11}'^2}{c_{11}^2} = \frac{\dfrac{L_4K_1\gamma_1c_1}{M_4K_4c_7^2} + \dfrac{L_2A}{c_7c_{11}} + \dfrac{L_6\gamma^2c_{10}}{M_6K_6c_7}}{\dfrac{c_{11}}{c_7} + \dfrac{L_1K_4M_4}{K_1M_1L_4}}. \tag{7}$$

In order to describe the behavior of electrodes of the *s o f t* glass assume

$$\frac{L_4K_1\gamma_1c_1}{M_4K_4c_7} \gg \frac{L_2A}{c_{11}} \quad \text{and} \quad \frac{L_4K_1\gamma_1c_1}{M_4K_4c_7} \gg \frac{L_6\gamma^2c_{10}}{M_6K_6},$$

which is equivalent to the statements: $c_8' \gg c_9'$; $c_8' \gg c_{10}'$. The physical significance of these conditions is roughly as follows: the ionic activity of the boundary layer between glass and water, which determines the behavior, is attributable in the main to the solute water and to the added base.[5] For the potential of the glass electrode we then obtain from (1) and (7) the expression

$$E_g = \frac{RT}{F} \ln \left[c_7\gamma \left(1 + \frac{K_1M_1L_4c_{11}}{K_4M_4L_1c_7} \right)^{\frac{1}{2}} \right] - \frac{RT}{2F} \ln \gamma_1c_1 + \text{const.} \tag{8}$$

and at *constant water activity*

$$E_g = (RT/F) \ln c_7\gamma + (RT/2F) \times \ln (1 + b(c_{11}/c_7)) + \text{const.} \tag{8'}$$
$$(b = K_1M_1L_4/L_1K_4M_4).$$

If the glass behaved like a hydrogen electrode, the following would be valid:

$$E_h = (RT/F) \ln c_7\gamma + \text{const.} \tag{9}$$

The difference between the two potentials is therefore

$$E_g - E_h = \Delta = (RT/2F) \times \ln (1 + b(c_{11}/c_7)) + \text{const.} \tag{10}$$

This quantity is termed by Dole the *error* of the glass electrode.

III. Comparison of Theory and Experiment

In order to bring the equation obtained into a form capable of being checked, we rewrite Eq. (10) as follows:

$$-y = \ln [(e^{2F\Delta/RT} - 1)/c_{11}\gamma] = \ln b + p_H. \tag{11}$$

That is to say, the function y must be linearly independent on the p_H with the slope of 1. We have tested this dependence of the function y on the p_H for all of Dole's experiments in which the solution contains sodium ions in addition to hydrogen ions. In order to depict the experiments made with the remaining salts (lithium, potassium and barium salts), our model would require to be expanded along the same lines since the glass employed by Dole was a sodium-calcium silicate. That is to say of the salts employed only the sodium salts have a cation in common with the glass to which our model applies. The theory was compared with Dole's observations on 0.05 molar sodium phosphate solutions, on unimolar sodium-chloride and acetate solutions and on 3.5 molar sodium acetate solutions. The activities of univalent ions in these solutions are obtained from tables[6] or by interpolation. We thus arrive at the following values for the activities of the sodium ion:

Na_2HPO_4	$a = 0.078$,	$c = 0.05$,
NaAc	$a = 0.77$,	$c = 1$,
NaCl	$a = 0.685$,	$c = 1$,
NaAc	$a = 3.57$,	$c = 3.5$.

With these values for the various activities the

[5] This method of dealing with solubility products in accordance with *experimental results* is criticized by Dole as being "highly artificial."

[6] *Landolt-Börnstein-Roth*, 5th Ed., 2nd Suppl., Vol. 2.

function y was calculated and plotted against p_H in Fig. 1. The points are freely grouped about a straight line with the slope of 1. No appreciable alteration in the slope occurs, except possibly in the solution poorest in sodium ions for which only *one* series was measured, but it should be noted that here the "errors" are only small as expected from the theory, and that the possibility of reproducing the potentials is limited.[7]

In order to check the numerical agreement of the theoretical formula, with *one* constant which describes *all* observations with *all* sodium concentrations, we shall calculate the same series as that which Dole tested his formula containing two constants. Note that Dole adapts the two constants of his formula as required to the observations of *one* series (constant sodium ion concentration), that is he employs six constants to represent all the measured points plotted in Fig. 1.

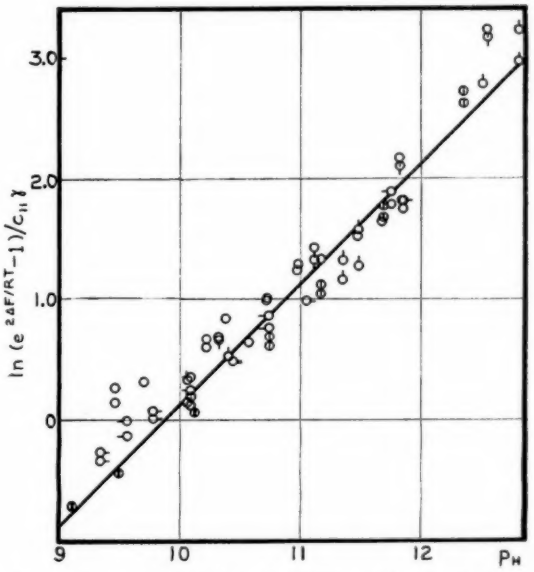

FIG. 1. Text of Eq. (11) $\ln[(e^{2\Delta F/RT}-1)/c_{11}\gamma] = \ln b + p_H$. ○ 0.05 Na_2HPO_4, ○- 0.9 NaAc+0.05 Na_2HPO_4, ◌ 1.0 NaAc, -○ 0.9 NaCl+0.05 Na_2HPO_4, ♀ 0.99 NaCl+0.01 NaAc, ⓘ 3.5 NaAc.

TABLE I. *Test of the Eq. (10). 0.9 c NaAc, 0.05 Na_2HPO_4.*

p_H	$\Delta_{obs.}$ *mV*	$\Delta_{calc.\ Dole}$	δ	$\Delta_{calc.\ (10)}$ $b=1.36\times10^{-10}$	δ	$\Delta_{calc.\ (10)}$ $b=1.23\times10^{-10}$	δ
9.34	4.3	4.3	0.0	2.6	1.7	2.4	1.9
9.78	7.6	7.4	0.2	6.3	1.3	5.8	1.8
10.44	15.6	15.7	0.1	17.3	1.7	16.4	6.8
11.05	27.6	28.2	0.6	32.7	5.1	31.4	3.8
11.84	50.5	44.3	6.2	55.1	4.6	53.8	3.3
			$(\overline{\delta^2})^{\frac{1}{2}}=2.8$		$(\overline{\delta^2})^{\frac{1}{2}}=3.27$		$(\overline{\delta^2})^{\frac{1}{2}}=2.6$

In the second column of Table I are given the "errors" found, and in the third column the "errors" calculated by Dole. The values for Δ given in the fifth column are calculated according to the Eq. (10), for which we have used the value for the constant $b=1.36\times10^{-10}$ which results from the graphic mean (Fig. 1) of the measurements at *all* sodium concentrations. As will now be seen, the agreement is almost as good as that obtained by Dole. A slight alteration of say 10 percent in our constant ($b=1.23\times10^{-10}$) would lead to agreement better than that obtained by Dole. If it be borne in mind that the constant b is of the nature of a solubility product, the slight uncertainty in the experiments of the different series is plausible. This is all the more so since the absolute potentials similarly differ from each other, presumably on account of uncheckable differences in the composition of the superficial layer. The agreement here obtained justifies the opinion that the proposed scheme is correct in principle, and useful for the description of the behavior of the glass electrode.

We will now turn to the second-mentioned deviations of the hydrogen electrode from a

[7] In certain series differences up to 10 mV occur at different electrodes immersed in the same solution. The potentials depend on the order in which the alkaline concentration is varied. (MacInnes and Belcher, J. A. C. S., 53, 3315 (1931).) According to Dole, the potentials obtained with the addition of potassium salts are also hard to reproduce. We wish to point out that all these observations are thoroughly consistent with our model, since the establishment of equilibrium in the superficial layer is a process which is not always effected momentarily.

TABLE II. *"Errors" through alteration of the water activity.*

% Ethanol	p_H	a_{H_2O}	$\Delta_{obs.}$	$\Delta_{calc.\ Dole}$	δ	$\Delta_{calc.\ (12)}$	δ
33	1.30	0.89	−1.3	−3.0	1.7	−1.5	0.2
33	0.41	0.89	−1.3	−3.0	1.7	−1.5	0.2
37	1.86	0.88	−2.0	−3.3	1.3	−1.7	0.3
55	1.36	0.83	−4.2	−4.8	0.6	−2.4	1.8
56	1.99	0.83	−4.6	−4.8	0.2	−2.4	2.2
66	0.71	0.79	−3.9	−6.1	2.2	−3.1	0.8
					$(\bar{\delta}^2)^{\frac{1}{2}}=1.46$		$(\bar{\delta}^2)^{\frac{1}{2}}=1.22$

glass electrode, taking into account the difference characterized by Dole. It may be taken to be thoroughly plausible to assume that the hydrogen ion in glass, as in water, is hydrated, while the dehydrated ion is discharged at the platinum-hydrogen electrode. The equilibrium between the two types of hydrogen ions in solution is given by the expression

$$c_7\gamma \times c_1\gamma_1/c_{H_2O} \times \gamma_{H_2O} = \text{const.}$$

There is a corresponding difference in the potentials of the two electrodes, which is dependent on the water activity and an "error," given by (cf. (8))

$$\Delta = (RT/2F) \ln c_1\gamma_1. \qquad (12)$$

In comparing theory with experiment, however, we may only proceed to such values for the activity of water as are permissible under the assumption that the water is still present as a solvent in great excess. This is so since all assumptions as to the activity coefficients relate to water as the solvent, and become entirely wrong when applied to other solvents. We therefore limit ourselves to water activities which are not lower than 0.79. In Table II we place the deviations found by Dole alongside those calculated by Dole himself and those calculated by us. As is evident from Table II, the agreement between the observed values and the calculated values by the authors is very fair, and better than the results of Dole's calculations, which are given in the fifth column of the Table II. It should be noted that by proceeding to very slight water activities we have gone beyond the range for which our theory is valid. The fact that the proposed model actually describes only the very slight deviations for water activities in the neighborhood of one, is not a peculiar weakness of the model, but is inherent in our lack of knowledge of the variation of the activity coefficient on change of solvent.

The Partial Pressures of Formic and Acetic Acids above Some Aqueous Solutions; and Their Partial Molal Free Energies at 1.0 Molal Concentration

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The paucity of data pertaining to the vapor pressures of aqueous solutions of the organic acids has hitherto retarded thermodynamic calculations in this field. In the present study the partial pressures of formic acid above three of its solutions and those of acetic acid above two solutions have been measured at 25°C. From these results the partial molal free energies at 1.0 molal concentration have then been derived.

Experimental Method

THE method employed was essentially similar to that which Bates and Kirschman[1] used in their investigation of the vapor pressures of the hydrogen halides in aqueous solution. It here involved the determination of the formic or acetic acid contained in a given quantity of nitrogen in equilibrium with the particular aqueous solution and a comparison of this with the amount of water vapor which the same sample of nitrogen contained when in equilibrium with pure water at the same temperature. From a knowledge of the vapor pressure of water (0.00313 atm. at 25°[2]) and the constants for the vapor-phase equilibria between the double and single molecules of the organic acid, the vapor pressures of the acids could then be computed.

The apparatus consisted of a train of saturators and absorbers through which nitrogen was passed; it was immersed in a thermostat at 25°C (±0.02°). In the successive parts of the apparatus the nitrogen sample was (I) saturated with vapor from the squeous solution that was being studied, next (II) passed through absorbers in which the acid vapor was absorbed by standard NaOH solution and later determined by titration, then (III) passed through saturators in which saturation with the vapor of pure water was completed, and finally (IV) passed through an absorber containing "Dehydrite" in order to determine this weight of water vapor. The usual precautions and tests[1] were made to insure the completeness of the saturation and absorption in the various parts of the gas train, and a correction was introduced for the change in volume of the nitrogen sample accompanying the small drop of pressure (9 mm of mercury) between the final saturator for the acid solution in I and the "Dehydrite" absorber in IV. Four to six acceptable determinations were made upon each of the solutions studied; the results of these determinations seldom differed from the mean values reported in Table I (column 2) by more than 2 percent, except in the case of the most dilute formic acid solution. Here, due largely to the low vapor pressure, the average deviation of the four values was 8 percent.

Vapor Pressure Data

The vapor pressure data are summarized in Table I. Column 1 contains the concentrations of the several solutions, expressed in mols of acid per 1000 g of water. The pressure values in column 2 are those computed directly from the quantities of acid and water found in the absorbers on the assumption that the molecular

TABLE I. *Vapor pressure data at 25°C.*

	Molality	P_f (atm.)	P_d (atm.)	P_s (atm.)
Formic acid	0.510	0.000115	0.000004	0.000108
	1.164	0.000245	0.000016	0.000214
	2.285	0.000476	0.000049	0.000378
Acetic acid	1.316	0.000345	0.000055	0.000235
	2.890	0.000830	0.000194	0.000441

[1] Bates and Kirschman, J. Am. Chem. Soc. **41**, 1991 (1919).

[2] International Critical Tables, Vol. III, p. 212.

weights of the acids are the same as their formula weights. Inasmuch as some of the acid molecules in the vapor state are polymerized or "double" molecules, this assumption is not true and accordingly these values are designated as fictional pressures (P_f). If P_s is the pressure of the simple or "single" acid molecules in the vapor, that of the double molecules becomes $P_d=\frac{1}{2}(P_f-P_s)$; and a condition of equilibrium between the two types of molecules must exist to satisfy the relationship $P_s^2/P_d=K_p$. Taking 0.0029 for the value of K_p for formic acid vapor from the work of Ramsperger and Porter[3] and 0.001 for K_p for acetic acid from the calculations of Parks and Huffman,[4] we have thus been able to deduce the values of P_d and P_s given in columns 3 and 4.

In the case of acetic acid our results for P_f differ by about 6 percent from those obtained recently by Fredenhagen and Liebster,[5] although our figures for P_s differ by a considerably larger amount because we have here employed a different value for K_p.

Some Derived Free Energy Data

With the aid of the preceding vapor pressure data and Henry's law we have estimated $P_s=0.000191$ atm. for 1.0 molal formic acid solution and $P_s=0.000184$ atm. for 1.0 molal acetic acid solution. Taking $P_s=0.0117$ atm. in the vapor above pure formic acid[3] at 25°C, we then find for the free energy change in the transfer of one formula weight of formic acid from the pure state into a 1.0 molal aqueous solution

$$HCO_2H\ (1)=HCO_2H\ (1.0m\ \text{aq.});$$

$$\Delta F_{298}=RT\ln 0.000184/0.0117=-2440\ \text{cal.}$$

Similarly, taking $P_s=0.004$ atm. in the vapor above pure acetic acid[4] at 25°, we have for the free energy of dilution of this acid

$$CH_3CO_2H\ (1)=CH_3CO_2H\ (1.0m\ \text{aq.});$$

$$\Delta F_{298}=-1820\ \text{cal.}$$

Our result for the free energy of dilution of formic acid differs by 520 calories from that ($\Delta F_{298}=-2960$) calculated by Ramsperger and Porter from Branch's data.[6] However, it should be noted that Branch worked with an aqueous solution of formic acid which was also 0.5 molal with respect to HCl and hence the dilution conditions are not quite comparable.

Combining these free energy changes with the values given by Parks and Huffman[7] for the free energies of formation of the pure liquid acids, we then obtain the partial molal free energies of the two acids in a 1.0 molal aqueous solution

$$C\ (\text{graph.})+H_2+O_2=HCO_2H(1.0m\ \text{aq.});$$

$$\Delta F^\circ_{298}=-87{,}590\ \text{cal.};$$

$$2C\ (\text{graph.})+2H_2+O_2=CH_3CO_2H(1.0m\ \text{aq.});$$

$$\Delta F^\circ_{298}=-96{,}320\ \text{cal.}$$

[3] Ramsperger and Porter, J. Am. Chem. Soc. **48**, 1267 (1926).

[4] Parks and Huffman, *The Free Energies of Some Organic Compounds*, p. 143, The Chemical Catalog Co., New York, 1932.

[5] Fredenhagen and Liebster, Zeits. f. physik. Chemie **A162**, 449 (1932).

[6] Branch, J. Am. Chem. Soc. **37**, 2316 (1915).

[7] Parks and Huffman, reference 4, p. 231.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Ultracentrifuge

We have previously described[1] a simple ultracentrifuge with which very high centrifugal forces were obtained. The method of rotating the centrifuge was a modification of that used by Henriot and Huguenard[2] in which very great stability and flexibility could be secured. The rotor was both supported and driven by a series of air jets in such a way that the maximum speed was limited only by the velocity of the air jets and the strength of the rotor.[1] In this work the centrifuge was applied to the study of suspensions of particles sufficient in size and relative weight to be separated in a comparatively short time and, as a result, the simple centrifuge chambers there described were quite satisfactory. However, recent experiments in the sedimentation of particles of molecular dimensions which sometimes require several hours centrifuging have necessitated changes in design in order to eliminate a slow remixing caused by convection currents. Since a convection current in a liquid is essentially a buoyancy phenomenon, any convection action is greatly magnified in solutions subjected to high centrifugal forces, i.e., in solutions subjected to centrifugal forces of several hundred thousand times gravity, very small temperature differences within the fluid will produce large convection currents. In the case of the air driven centrifuge the bottom part of the rotor is kept cooler than the top part due to the expanding air jets below and the air friction, etc., above. It was, therefore, necessary to design a centrifuge chamber that would eliminate these troublesome temperature gradients. After some schemes, such as previously warming the air, etc., were found to be impractical, this was accomplished by some rather simple changes in the design of the rotor. The depth of the centrifuge chamber was reduced to about 0.6 mm and bounded at bottom and top by specially prepared strong glass disks[1] sealed around the periphery with soft DeKhotinsky. Just below the centrifuge chamber a deeper chamber was provided which could be filled with a liquid to act as a temperature equalizer. Liquids with high temperature coefficients such as turpentine are preferable for this purpose because of the temperature equalization by their own convection action, but usually some of the solution being centrifuged will serve the purpose. With this arrangement the trouble arising from convection currents has been eliminated so that the centrifuge may run for many hours without appreciable remixing, e.g., hemoglobin molecules have been separated from the clear fluid with the above arrangement utilizing centrifugal forces of only about 10^5 gravity. To increase the capacity of the centrifuge, several centrifuge chambers may be placed one above the other or a large chamber may be divided into a series of thin partially insulated layers.

In order to collect both the lighter and heavier portions of the substance being centrifuged, a slightly heavier nonmiscible liquid should be used to displace the lighter fractions in a way previously described.[1] In these methods it is preferable to provide means of conducting the displacing liquid to the periphery without its passing through the solution to be collected. The liquid should not be too heavy or introduced too rapidly as stirring will occur. Sugar solutions may be used for substances where the lighter fractions only are to be saved.

Another phase of the work has been the development of small centrifuges to give very high centrifugal forces. With a rotor 9 mm in diameter driven by four jets of hydrogen (pressure 160 lbs. per sq. in.) instead of air a rotational speed in excess of 20,000 r.p.s. was obtained. This rotational speed produces a centrifugal force of about seven million times that of gravity, on the periphery of the rotor. These small centrifuges should be especially suitable for the microscopic observation of small particles in intense centrifugal fields by methods similar to those of Harvey.[3] A simple way of measuring the rotational speed is to view a white dot near the periphery of the rotor in a rotating mirror above the stator, preferably by means of a telescope.

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February 1, 1934.

[1] See Science **78**, 338 (1933) for details of construction and other references.

[2] Henriot and Huguenard, J. de Phys. et Rad. **8**, 443 (1927).

[3] Harvey, J. Frank. Inst. **214**, 1 (1932).

* Charles A. Coffin Fellow.

Phase Boundary Potentials of Monolayers of Long-Chain Fatty Acids

By means of the electrical method of measuring the phase boundary potentials (ΔV) of monolayers of long chain fatty acids described by Schulman and Rideal[1] we have investigated in some detail the behavior of the stable and metastable liquid expanded and the liquid condensed states of myristic acid. The experimental data reported by the above authors,[1] by Adam and Harding[2] and by Harkins and Fischer[3] are not in agreement and indeed doubt has been cast upon the existence of the metastable liquid expanded state and its transition into the liquid condensed state.

On compressing a liquid expanded film to areas between 40A² and 20A² per molecule a high phase boundary potential is observed which falls with time. The film is evidently metastable in respect to its contribution to the phase boundary potential. During this fall of ΔV the film is heterogeneous as can be readily verified by exploration of the surface. After waiting 4–5 hours when the molecular area is about 25A² the film becomes homogeneous, but when the area is 38A² it remains inhomogeneous. These experiments strongly support the micellar structure for the film as proposed by Langmuir.[4] This apparent change in the properties of the film appears to us to be most readily interpreted on the view that during the fall of potential water is being squeezed out from between the chains themselves. This process of elimination of water can be accelerated by the addition of tannic acid to the underlying solution when equilibrium is found to be established in a much shorter period of time (1½ to 2 hours). Since the bulk solubility of the acid in the metastable liquid expanded state appears to be higher than that in the liquid condensed state and the solubility can be reduced both by saturation of a 0.01 N HCl substrate with myristic acid and also by the use of 0.1 N HCl as substrate we conclude that in addition to the hydrocarbon adhesion emphasized by Langmuir both the hydration of the chain and the properties of the polar head group are important fundamental factors for the existence of the film in these states.

N. W. H. Addink
Eric K. Rideal

Laboratory of Colloid Science,
Cambridge, England,
February 5, 1934.

[1] Schulman and Rideal, Proc. Roy. Soc. **A130**, 259 (1930).
[2] Adam and Harding, Proc. Roy. Soc. **A138**, 411 (1932).
[3] Harkins and Fischer, J. Chem. Phys. **1**, 853 (1933).
[4] Langmuir, J. Chem. Phys. **1**, 756 (1933).

The Relative Reactivities of the Hydrogen Isotopes with Chlorine

It has been shown recently[1] that if mixtures of hydrogen, chlorine, and carbon monoxide are illuminated with light absorbed by the chlorine, the relative amounts of phosgene and hydrogen chloride formed are governed by the equation

$$(\Delta H_2+\Delta CO)/\Delta H_2=1+k(CO)/(H_2). \qquad (1)$$

The left-hand member of this equation is equal to the reciprocal of the fraction of the chlorine which reacts with hydrogen; on the right-hand side the pressures of carbon monoxide and hydrogen in the reaction mixture are substituted. The constant, k, is the ratio of the specific rate constants of the reactions of the two gases with the active form of chlorine, and is equal to the reciprocal of the value of the ratio $(CO)/(H_2)$ for which the quantity $(\Delta H_2+\Delta CO)/\Delta H_2$ is equal to two. This relationship offers a convenient method of comparing the relative reactivities of the two isotopes of hydrogen as the ratio of the values of k obtained by using ordinary hydrogen and the heavy hydrogen gives the ratio of the specific rate constants of these two isotopes for the particular reaction involved in this system. This method has the very great advantage that the results are not affected by inhibitors and therefore are more accurate than could be obtained by rate experiments.

The carbon monoxide and chlorine were prepared as in the previous work.[1] The heavy hydrogen was prepared from heavy water (obtained from Professor G. N. Lewis) by treatment with metallic sodium. This is the usual procedure followed in this laboratory and it has been found that all the hydrogen is liberated from the water if the sodium is heated to approximately 300°C. The apparatus and experimental procedure were the same as previously described.[1]

The difference in the behavior of the two isotopes is quite marked. Whereas with ordinary hydrogen at 0°C it is necessary to have nearly four times as much carbon monoxide as hydrogen in order to have the chlorine divide equally between the two, with heavy hydrogen nearly four times as much hydrogen as carbon monoxide is needed. In Table I are given the values of $(CO)/(H_2)$ for which $(\Delta H_2+\Delta CO)/\Delta H_2=2$. From Eq. (1) it is apparent that these are the values for the specific rate constants of the two hydrogen isotopes expressed in terms of the rate constant for the reaction of chlorine with carbon monoxide. In order to obtain as accurate values as possible from the data two graphs were made from each set of data, one being a plot of $(\Delta H_2+\Delta CO)/\Delta H_2$ against $(CO)/(H_2)$, the other $(\Delta H_2+\Delta CO)/\Delta CO$ against $(H_2)/(CO)$. The former emphasizes the errors in the measurement of ΔH_2 and the latter those for ΔCO. This method resulted in lowering the value 3.9 previously given for ordinary hydrogen at 0°C to 3.7 is given in the table. This change is within the limits of accuracy of the experiments which is about ten percent, because of errors in measuring the small changes.

Applying the Arrhenius equation, we may write

$$k_2/k_1=(s_1/s_2)e^{-(Q_1-Q_2)/RT}.$$

As we have the values of k_1/k_2 at two temperatures, we may

[1] Rollefson, J. Am. Chem. Soc. **56**, March (1934).

TABLE I.

Temperature	H_2 k_1	H^2_2 k_2	$\frac{k_1}{k_2}$
0°C	3.7	0.275	13.4
32°C	16.6	1.70	9.75

calculate Q_1-Q_2 and s_1/s_2. The values obtained are $Q_1-Q_2=-1630$ cal. and $s_1/s_2=0.66$. If the two types of hydrogen molecules are assumed to have the same collision diameters and the same steric factors, s_1/s_2 should be $2^{\frac{1}{2}}$. The difference between this value and that calculated from the data is not considered of any significance as an error of ten percent in one of the experimental ratios corresponds to a change in Q_1-Q_2 of 540 calories and a change in s_1/s_2 of a factor of 2.7. We may conclude therefore that the molecules of heavy hydrogen are less reactive than those of ordinary hydrogen in the reaction to form hydrogen chloride due to the fact that the reaction involving the former has a slightly higher heat of activation.

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February 8, 1934.

The Energies of the Atomic Linkages in Methane, Ethane, Methanol and Ethanol[1]

Data recently obtained in this laboratory on heats of combustion lead to the following values for the change in heat content associated with the addition of $\frac{1}{2}O_2$ to methane and ethane to form methanol and ethanol, respectively:

$$CH_4(gas)+\tfrac{1}{2}O_2(gas)=CH_3OH(gas),$$

$$\Delta H^\circ_{298}=-30.24\pm0.09;$$

$$C_2H_6(gas)+\tfrac{1}{2}O_2(gas)=C_2H_5OH(gas),$$

$$\Delta H^\circ_{298}=-36.09\pm0.15;$$

kcal. per mole.

These data show that the energy of the process of breaking a C−H bond in the molecule $R-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H$ and inserting an oxygen atom to form the molecule $R-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-O-H$ is appreciably affected by the nature of the substituent R; and that, contrary to what has been assumed by practically all investigators in this field, the energies of the atomic linkages in these and homologous compounds are quite significantly not additive.

In a subsequent paper which will appear in the *Bureau of Standards Journal of Research*, it will be shown that even in the normal paraffin hydrocarbons the energies of the atomic linkages are appreciably affected by the nature of the substituents, hydrogen atoms or alkyl groups.

FREDERICK D. ROSSINI

Bureau of Standards,
Washington, D. C.,
February 8, 1934.

[1] Publication approved by the Director of the Bureau of Standards, United States Department of Commerce.

Direct Experimental Measurement of Electron Affinities

The electron affinity of an electronegative gas, ΔE at 0°K of the reaction $X^-\rightarrow X+e^-$, may be readily calculated if the equilibrium constant of the above reaction can be measured. If the gas X_2 at low pressure is allowed to come in contact with a hot metallic surface (thermionic emitter), molecules X_2, atoms X, electrons e^-, and ions will leave the surface. If it is assumed that the relative amounts of the various molecular species leaving the surface are independent of the temperature of the molecules X_2 hitting the surface, that is if complete equilibrium on the surface exists, then the equilibrium pressures and the electron affinity may be simply calculated from the numbers of X^-, X, and e^- leaving the surface. In the case of iodine, calculations predict, and observations show,[1] that at above 1500°K the molecules are completely dissociated into atoms, and since a very small fraction of the atoms are converted into ions on a tungsten surface, the number of atoms leaving the surface will be twice the number of impinging molecules. The necessary data for the calculations are then, the temperature of the surface, the pressure of the gas X_2 in the vessel, and the ratio of the currents carried by the ions and electrons.

By using, in a cylindrical arrangement, a tungsten filament (0.2 mm diam. 0 volts) a wire net grid (10 mm diam. about+10 volts) and a cylindrical plate collector (40 mm diam. about+15 volts) inside a solenoid producing a magnetic field parallel to the axis of the cylinder, the electron current from the filament can be completely deflected from reaching the plate at fair solenoid currents even in the presence of considerable gas pressure. (Magnetron set-up.) The heavy ions I^- are unaffected by the magnetic field. The voltage necessary to obtain saturation

[1] Communication from Dr. Irving Langmuir.

TABLE I.

Filament temperature (°K)	Iodine pressure $\times 10^{-3}$mm	Currents in arbitrary units Ion	Electron	Electron affinity (kcal.)
1813	0.35	2.3	213	76.7
1886	0.92	14.4	930	76.1
1887	1.8	20.5	2450	71.6
1891	0.28	9.5	1320	78.3
1892	1.5	19.3	2430	72.4
1968	1.4	116.	15300	75.5
2031	1.8	560.	53000	78.6

currents can also be used as auxiliary measurement of the ion current.

A few preliminary measurements are reported in Table I. The results,* although capable of much greater refinement indicate values in good agreement with other methods,[2] 74.2 kcal. being calculated from the theoretical lattice energies of the alkali iodides.

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February 9, 1934.

[2] J. E. Mayer and L. Helmholz, Zeits. f. Physik **75**, 19 (1932). J. E. Mayer, Zeits. f. Physik **61**, 798 (1930).

* The calculations assume no reflection of electrons, ions or atoms from the filament. The experimental electron emission of tungsten suggests a possible electron reflection coefficient 0.5;* assuming this would decrease our electron affinities by about 2.5 kcal.

The Raman Spectrum of Lead Tetramethyl

We have been investigating the Raman spectra of a group of metallo-organic compounds. In this letter we will give some results we have obtained with lead tetramethyl.

The lead tetramethyl was distilled *in vacuo* into the Raman tube. The spectra were excited by the blue and violet mercury lines separately by using an apparatus described by one of us with D. H. Andrews.[1] The following lines were found: 135 (8br), 458(10), 472(8), 766(1/2), 930(0), 1155(3), 1169(2), 2921(8), 3000(3). The 2921 and 3000 lines are assigned to vibrations in which the C−H bond is stretched. The 930 line is probably an harmonic of 458. The remaining lines may be assigned to the bending and stretching motions of a pentatomic molecule whose structure is probably tetrahedral. The three lowest are probably due to bending and the others to stretching.

It is of interest to note that there are two pairs of close doublets of considerable intensity, and that the line at 135 cm^{-1} is broad and unsymmetrical, which suggests that it is also a doublet. The assignment of frequencies to types of vibrations is thus rather uncertain. The low intensity of 766 renders its association with the symmetrical motion improbable, but it is difficult to reconcile the doublet structure of the other frequencies with this kind of motion. The apparent absence of the line at 1450, which usually occurs in compounds containing the methyl group, is also of interest.

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February 14, 1934.

[1] D. H. Andrews, J. Chem. Phys. **1**, 406 (1933).